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A NEW GRAVIMETRIC METHOD FOR THE DETERMINATION OF THE NITRITE ION USING NITRITON-B (o-AMINOANILIDE OF BENZENESULFONIC ACID)

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During studies of the interaction of NO_2^- ions with the o-aminoanilide of benzenesulfonic acid, which we tried to use instead of the less readily available o-anilide of diphenic acid (Nitriton A) [1], it was found that the white turbidity, which appears on pouring the solutions together, very rapidly changes over into a coarse crystalline precipitate. In this sense, Nitriton B behaves like substances whose solubility changes considerably with crystal size, while the white turbidity which Nitriton A forms with nitrite ions, does not possess this property.

Preliminary experiments showed that Nitriton B practically completely precipitates NO_2^- ions according to the reaction

$$\langle\!\!\!\rangle-SO_2-\overset{H}{\underset{|}{N}}-\langle\!\!\!\rangle\overset{H_2N}{} + HNO_2 = \langle\!\!\!\rangle-SO_2-\overset{|}{N}-\langle\!\!\!\rangle\overset{N=N}{} + 2H_2O,$$
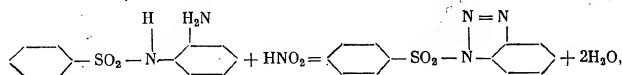
leading to the formation of benzenesulfanyl-o-phenylenediazimide (atriazole). This precipitate, as indicated above, satisfies the requirements normally met in gravimetric analysis. This fact persuaded us to study the possibility of using this reaction for the direct gravimetric determination of nitrite. This problem proved of particular interest in view of the fact that hitherto no method has been published for the gravimetric determination of nitrite ions.

NaNO$_2$ Solution. The solution was prepared from chemically pure grade material, which was given a preliminary wash with boiled water;it was isolated from air by means of two washers, one of which contained a solution of KOH 1:2, while the other contained a mixture of one volume of KOH 1:2 and one volume of pyrogallol 1:5. NO_2^- concentration was checked by means of permanganate.

Nitriton B Solution. 2.480 g of the o-aminoanilide of benzenesulfonic acid was dissolved in 1 liter of 0.2 M H_2SO_4. The solution can be stored.

All the dilutions were carried out in calibrated measuring apparatus to ensure errors of not more than 0.2%.

Preliminary tests were carried out over a wide pH range for 3.0 to 8.5. It was found that at a pH of 8.5, in general, no precipitate of the triazole was formed; neither was any formed at lower pH values until 3.5 was reached, at which it was first detected. Within this pH range the reaction for NO_2^- remained quite positive. Only at a pH of ≤ 3 was quantitative separation of NO_2^- ions from solution achieved; at a pH of ≤ 1.5 however, together with precipitate formation, the odor of nitrogen oxides could be detected, indicating the danger of loss of NO_2^- ions. In this connection, further work was carried out in the pH range 1.5-2.8, with slow addition of reagent to the solution to be tested and efficient agitation. It was found, in addition, that complete

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precipitation of NO_2^- ions was achieved when 1.5 moles of Nitriton B was used per 1 g-ion of NO_2^- ions. When all these conditions were satisfied, precipitation was complete in 10-15 minutes.

Determination of nitrite ions in solution was carried out as follows. A known amount of $NaNO_2$ solution was pipetted into a 100 ml beaker, and Nitriton B solution added dropwise. In order to maintain the pH at 1.5-2.8, the solution was diluted with water and the necessary amount of 1 M Na_2CO_3 solution added. The total volume of solution in all tests was about 75 ml. After standing for 8 hours in the dark, the precipitate was filtered off in a sintered glass crucible No. 4. The precipitate was washed with 5-10 ml of 0.1 M H_2SO_4, then 6 times with cold water, and dried to constant weight in the apparatus shown in Fig. 1, which was fitted up in a drying oven heated to 75°. As can be seen from Fig. 1, crucible 1 is fitted in a hole cut in a rubber plug 2 and is covered with a glass adapter 3, in the spherical bulb 4 of which is fitted a plug of glass wool. A calcium chloride drying tube is fused directly on the adapter 3, this tube being filled with calcium chloride and stoppered with plug 6, through which passes a tube 7 connected to a large column filled with $CaCl_2$ located outside the drying oven. To the end of the air outlet tube 8, sticking out of the drying oven is fitted a Drechsel bottle containing sulfuric acid which could be used as a bubble counter. In operation air was sucked through at the rate of a bubble per second. Using such an apparatus, the precipitate could be dried in 20 minutes instead of 1.5 to 2.0 hours which would be spent if drying were carried out using ordinary drying conditions in a drying oven.

Experimental results which have been treated statistically [2], are given in Table 1, the reliable level was $a = 0.95$; they were calculated by means of the stoichiometrically obtained conversion factor $F = 0.1774$ (log $F = 1.2491$). As is evident from Table 1, the method gives completely satisfactory results.

Qualitative tests showed that in the pH range 3.5 to 1.0, within which limits the NO_2^- ion is precipitated, Nitriton B only forms white crystalline precipitates with Ag^+, Hg_2^{2+} and Hg^{2+}.

When such oxidizing agents as MnO_4^-, $Cr_2O_7^{2-}$, IO_3^-, $S_2O_8^{2-}$ and Fe^{3+} were tried out against Nitriton B, and ClO_3^- solutions both in the cold and on warming, an orange color developed when large amounts of the oxidizing agents were present, and a rose color when small amounts were present. High concentrations of oxidizing agent gave on heating a dark orange precipitate, which on further oxidation, became paler, maintaining a yellowish color. In alkali media, oxidizing agents color the Nitriton B solution differently, from yellow-green to cherry-red. On acidification of an alkaline solution, the yellow-green color changes to red-orange. The transition range extends from pH 5.2 to 5.6.

Fig. 1. Apparatus for drying the precipitate.

TABLE 1

Gravimetric Determination of NO_2^- by Means of Nitriton B

NO_2^- taken in mg	Number of determinations	NO_2^- found in mg $\bar{c}$	$\Sigma (c_i - \bar{c})^2$	s^2 *	$s_{\bar{c}}$ **	$t_{0.95} \cdot s_{\bar{c}}$
10.0	10	10.05	0.110	$1.1 \cdot 10^{-2}$	$3.5 \cdot 10^{-2}$	± 0.08
15.0	10	15.02	$3.4 \cdot 10^{-2}$	$3.4 \cdot 10^{-3}$	$2.0 \cdot 10^{-2}$	0.04
20.0	10	20.04	$6.9 \cdot 10^{-2}$	$6.9 \cdot 10^{-3}$	$2.8 \cdot 10^{-2}$	0.06
30.0	10	30.07	0.168	$1.7 \cdot 10^{-2}$	$4.3 \cdot 10^{-2}$	0.10

$$* \ s^2 = \frac{\Sigma (c_i - \bar{c})^2}{n}. \qquad ** \ s_{\bar{c}} = \frac{s}{\sqrt{n-1}}$$

Thus, it seems that Nitriton B may be regarded as a specific precipitating reagent for the nitrite ion, since Ag^+, Hg_2^{2+}, and Hg^{2+} ions are rarely met with at the same time as NO_2^- ions.

Further studies of the properties of the triazole precipitate showed that it will withstand temperatures not exceeding 75° for long periods without changing weight or outward appearance. At 90-110° the white crystals of the triazole gradually acquire a rose color and then become orange; simultaneously the weight increases. This precipitate partially dissolves in water to give a red colored solution. The white residue which is insoluble in water is the normal triazole; it does not dissolve in 0.1 M H_2SO_4 but dissolves completely in 0.1 M NaOH; on subsequent acidification of the alkali solution, no precipitation occurs. Solutions of triazole in sodium hydroxide have the following properties: on heating, or long standing, they become yellow if the triazole concentration is low; oxidizing agents (CrO_4^{2-}, IO_3^-) also color them yellow; on oxidation of triazole solutions acidified beforehand, a rose color develops. The capacity of triazole to give colored products on oxidation was used for the colorimetric determination of its solubility in water.

A calibration curve was constructed: 0.2590 g triazole was dissolved in 50.00 ml 0.1 M NaOH with gentle warming; the solution was neutralized with H_2SO_4 and diluted with 0.1 M H_2SO_4 to 1 liter; triazole concentration in this first solution was $1.00 \cdot 10^{-3}$ M/liter; 25.00 ml of first solution was diluted with same solution of 0.1 M H_2SO_4 to 500 ml; the concentration of this second solution was $5.00 \cdot 10^{-5}$ M/liter; aliquots of this second solution were measured out by means of a micro-buret into a 50 ml flask, 5 ml of $5.0 \cdot 10^{-3}$ M KIO_3 added, and the volume made up to 35 ml with 0.1 M H_2SO_4; this solution was heated 5 minutes, allowed to stand 12 hours in the dark at room temperature, made up to 50 ml with water, and the optical density measured on an FEK-M colorimeter.

The calibration curve proved to be a straight line:

$$c = 1.925 \cdot 10^{-6} + 1.373 \cdot 10^{-4} D,$$

where c is the desired triazole concentration, while D is the corresponding optical density.

Determination of the solubility of triazole in water was carried out as follows: an aliquot of the Nitriton B solution was precipitated with a small excess of $NaNO_2$ solution; the precipitate was washed first with 0.1 M H_2SO_4 to a negative reaction for NO_2^- ions, then with water to remove SO_4^{2-} ions; the washed precipitate was transferred to a flask to which was added 500 ml of water, and the whole allowed to stand in the dark with frequent agitation; after 5 days, 250 ml of filtrate was taken and evaporated on a water bath to ~ 30 ml, which was transferred to a 50 ml standard flask; 5 ml of $5.0 \cdot 10^{-3}$ M KIO_3 solution prepared in 0.1 M H_2SO_4 was added, and after a five minute heating on a boiling water bath, the solution was left for 12 hours in the dark at room temperature; after dilution of this solution to the mark (50 ml) with water and mixing, its optical density was measured photocolorimetrically and the triazole concentration determined by means of the graph. The solubility of triazole determined in this way by 10 measurements was found to be equal to

$$(3.0 \pm 0.3) \cdot 10^{-6} \text{ M/liter,}$$

at a reliable level of $\overline{0}.95$; this corresponds to a loss of 0.138 mg NO_2^- ion per liter of solution.

Two further series of tests were carried out to ascertain the errors arising on precipitation of the triazole in the presence of other ions. Results of these tests are given in Table 2, where Series No. 1 includes determinations of nitrite ion in a solution, 1 liter of which contained at the same time $1.0 \cdot 10^{-2}$ M solutions of each of the nitrates of zinc, cadmium, magnesium, manganese, aluminum, and potassium; while Series No. 2 included determinations of nitrite ion in a solution, 1 liter of which contained at the same time $1.0 \cdot 10^{-2}$ M solutions of Na_2AsO_3, Na_2HPO_4, $Na_2B_4O_7$, KCNS, NaBr and KNO_3. Precipitation of the NO_2^- ion was carried out in each case at a pH of 1.5.

Further, an attempt was made to use the method under discussion for controlling the composition of nitrite baths widely used in our industry for burnishing metals [3]; they usually have the following composition:

NaOH 500-150 g/liter of water
$NaNO_3$ 200-250 g/liter of water
$NaNO_2$ 50-250 g/liter of water.

TABLE 2

Determination of NO_2^- by means of Nitriton B in Solutions Containing Other Ions:
In particular, in Solutions Corresponding in Composition to Baths Used for Burnishing Metals

Series number	NO_2^- taken in mg	Number of analyses	NO_2^- found in mg	$\Sigma (c_i - \bar{c})^2$	s^2	$s_{\bar{c}}$	$t_{0.95} \cdot s_{\bar{c}}$
1	23.0	6	23.03	0.2095	$3.5 \cdot 10^{-2}$	$8.4 \cdot 10^{-3}$	±0.22
2	37.5	6	37.52	$9.21 \cdot 10^{-2}$	$1.5 \cdot 10^{-2}$	$5.5 \cdot 10^{-3}$	0.14
3	34.5	6	34.52	$5.14 \cdot 10^{-2}$	$8.6 \cdot 10^{-3}$	$4.1 \cdot 10^{-3}$	0.11
4	57.5	6	57.49	$6.23 \cdot 10^{-2}$	$1.0 \cdot 10^{-3}$	$4.6 \cdot 10^{-3}$	0.12
5	75.0	6	75.06	0.852	0.14	0.17	0.44

During burnishing, which is carried out at a temperature of 135-150°, alloy components are oxidized and fall as hydroxides into the sludge; in the supernatant electrolyte their concentration is very small. In this connection, the following concentrations were used, 1 liter contained 3.3 g of Na_2SO_4, 0.5 g $NaNO_3$, and $4 \cdot 10^{-4}$ M of $Fe_2(SO_4)_3$, $Cr_2(SO_4)_3$, $NiSO_4$ and $MnSO_4$. These concentrations correspond to a sample from a bath diluted 400 times, while, as special experiments showed, the contents of the heavy metals were considerably higher than those met normally in practice. To 100 ml of such a solution was added a definite amount of $1 \cdot 10^{-2}$ M $NaNO_2$; it was then determined as follows: a saturated sodium carbonate solution was added to precipitate the heavy metals, the precipitates were filtered off and washed with 1% Na_2CO_3; the filtrate was neutralized with 1 M H_2SO_4 using litmus paper as indicator, nitrite was then precipitated by using sufficient Nitriton B, the triazole being determined gravimetrically as described. In all, three series of tests were carried out — Nos. 3-5; the results obtained proved completely satisfactory; they are given in Table 2.

TABLE 3

Determination of NO_2^- in Cases Where the Triazole is Precipitated by Gradual Acidification of an Alkali Solution Containing Excess Nitriton B

NO_2^- taken in mg	Number of determinations	NO_2^- found $\bar{c}$ in mg	$\Sigma (c_i - \bar{c})^2$	s^2	$s_{\bar{c}}$	$t_{0.95} \cdot s_{\bar{c}}$
35.0	5	38.03	5.71	1.14	0.53	±1.47
25.0	5	27.99	4.44	0.89	0.47	1.31
10.0	6	10.76	3.12	0.52	0.32	0.82

Since, in some instances, there are materials containing the nitrite ion, which give solutions with pH > 7, we checked on the possibility of precipitating the triazole by gradual acidification of such a solution, containing an excess of Nitriton B added beforehand, to a pH of 1.5-2.8. The results obtained which are given in Table 3 show poor reproducibility, since the dispersion s^2 is very high, and, in each case, in the first two series, no doubt includes systematic errors, since the range $\bar{c} \pm t_{0.95} s_{\bar{c}}$ does not include the true value of the NO_2^- ion concentration.

The results given above enable us to recommend the procedure described above — by means of which the results given in Table 1 were obtained — for the gravimetric determination of nitrite ions using Nitriton B. Apparently, this method can be used in many instances, in particular for determination of NO_2 in pickles used in the food industry [4]; it is especially suitable in this case, since the polarographic method recommended for this purpose gives satisfactory results only when a number of precautions are taken.

SUMMARY

1. A new gravimetric method has been developed for the determination of nitrite ions as benzene-sulfanyl-o-phenylenediazimide (atriazole), which is formed by the interaction of NO_2^- with the o-aminoanilide of benzenesulfonic acid (Nitriton B).

2. The properties of Nitriton B have been studied, as well as those of the triazole formed by its interaction with NO_2^- ions; in particular, the solubility of the triazole in water has been determined.

3. Conditions for precipitation have been determined which assure getting best results in the presence of other ions, and an analytical procedure has been worked out.

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* T. p. = C. B. Translation pagination.

A MICROFLOTATION METHOD OF ANALYZING HEAVY WATER

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For isotopic analysis of water with a low content of heavy isotopes of hydrogen and oxygen, the method most widely used is the flotation method [1], which gives an accuracy of ~1%, but requires not less than 2-3 g of water. Accordingly, several micro methods have been developed, of which the most widely used is the micro-flotation method proposed in 1933 by Gilfillan and Polanyi [2]. This method consists in measuring the pressure at which a state of flotation is achieved for a float immersed in standard water, this float having an elastic head and a reservoir which is filled through a narrow opening with test water; the density of this water is found from the value of the flotation pressure by means of a calibration curve relating flotation pressure to the density of the water in the float; the curve in turn is drawn by determining the flotation pressure for a float successively filled with several samples of water of known density. A few tenths of a ml of water is required for analysis; its accuracy is 2-3%.

This method has the following essential drawbacks: 1) the elastic properties of the float head change rapidly; this means frequent calibration; 2) the relation between the density of the water with which the float is filled, and flotation pressure is non-linear in character; this complicates calibration; 3) it is difficult to determine flotation pressure sufficiently accurately, since it depends on several parameters; 4) it is necessary to carry out calibration and all analyses at the same temperature, exact establishment of which in thermostats of the usual type is difficult.

In the present article we have described a modification of the Gilfillan and Polanyi method, in which a non-resilient float of the type depicted in Fig. 1 is used, while the state of flotation is achieved as in normal flotation methods, by changing temperature and not pressure. When such modifications are used, the drawbacks enumerated above are eliminated.

For isotopic analysis of water by our method, flotation temperatures T_1 and T_2 are found for the float filled with standard water and with test water respectively, when the float is immersed in each case in standard water. Afterwards, by means of tables for changes of density of water with temperature, we determined the increase in density Δd_{outer} of the water, in which the float is immersed, on changing the temperature from T_1 to T_2. The value of Δd_{outer} is related to the sought for excess density Δd of the test water (as compared with the standard water). This relation is determined as follows. A float of total volume V, partly filled to volume v with water of density d_1, and immersed in water of density D_1, floats at a temperature T_1. In order to achieve a new state of flotation after filling the float with water of different density (d_2), it is necessary to change the temperature to T_2. When this is done, the density of the water outside the float changes to D_2, while the density of the water in the float changes to $d_2 + (D_2-D_1)$. The new state of flotation is achieved when the change in weight of the float and the water filling it becomes equal to the change in the weight of water displaced by it, i.e. when

$$V\left[(d_2 + D_2 - D_1) - d_1\right] = V\left(D_2 - D_1\right)$$

or

$$\Delta d = \Delta d_{outer} \cdot \left(\frac{V}{v} - 1\right) = \Delta d_{outer} \cdot K. \tag{1}$$

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The coefficient K* is determined experimentally by determining the value of Δd_{outer} for one sample of water with a given Δd.

It is evident from Equation (1), that the absolute error in determining Δd is equal to the error in determining Δd_{outer}, multiplied by K. When K < 1, this error can, in principle, become less than that in the usual flotation method, and becomes smaller, the smaller K**. The use of this ratio for further increasing the accuracy of the flotation method of water analysis is not excluded.

Description of the Method

Construction of Float. The floats which we used (20-30 mm long) are depicted in Fig. 1. It is clear from Equation (1) that the value of coefficient K is smaller, the nearer to unity the value of the ratio V/v. In order to get a favorable value for this ratio, the floats were made with thin walls (but not so thin that they became sensitive to pressure variations). Chemically stable glass capillaries 1.5-2 mm in diameter with a wall thickness of ~ 0.1 mm proved suitable for constructing the floats. The top and bottom parts of the float were made separately with long drawn out pieces as shown in Fig. 2a, and then fused together. An opening of diameter 0.03-0.05 mm was made by rotating in the flame the evenly cut end of the lower part of the float fused to the other end until the opening ceases to be visible. The size of the opening was controlled by measuring with a microscope. The dimensions of the top and bottom part of the float were chosen so that the float, when filled with standard water, floated in the same water, (i.e. in some more standard water) at a temperature 5-6° higher than room temperature. A bit of glass is taken off or put on the float in order to adjust it for the required temperature. A convenient length for the shaft is 50-60 mm (Fig. 2b), so that it can be heated without expulsion of water from the float. The shaft is only given its final shape after completion of adjustments.
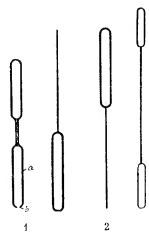
Cleaning, Storage, and Handling of the Float. The float is washed with a freshly prepared solution of $KMnO_4$ in concentrated sulfuric acid and carefully rinsed with clean water. Wash liquor will enter on immersing the float warmed in hot water in it*.**. Forceps made from elastic steel wire and with platinum tips, as shown in Fig. 3 are used for handling the float for washing purposes.

Floats are stored as shown in Fig. 4 and are handled by means of the platinum hook also shown in the diagram.

Fig. 1. Floats for micro-flotation analysis of heavy water.

Figs. 2a and 2b. Order in which construction operations were carried out.

Purification of Water for Analysis. 0.03-0.05 g of water sample is placed in the test tube a of the apparatus shown in Fig. 5, and frozen with liquid air; the apparatus is then evacuated to a pressure of 1-3 mm Hg. Tap b is closed and the water heated to 30-40°, its vapors pass into a quartz tube c, 45 cm long heated to 800°; this tube is filled with cupric oxide; the vapors condense in the cooled tube d which contains a few mg of Ag_2O for neutralization. The water is then driven from tube d into tube e containing the float. Two discs f of sintered glass prevent dust from the air and from cupric oxide from falling into e. Trap g cooled with liquid air holds back any oil vapors from the pump. Thick vacuum grease is put on all the ground glass joints.

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* The ratio V/v, which determines the value of K, does not depend on the temperature despite the fact that the values of V and v depend on temperature.

** Inaccuracy in the value of K does not play a part in determining the excess density of one water sample as compared with another, which usually interests research workers; accordingly, we did not take it into account.

*** We took into account thermal fatigue of the glass by checking, on the day analyses were made, the flotation temperature of the float, filled with standard water; it has no effect on the value of coefficient K.

The purification scheme just described is only suitable for water containing excess deuterium. For heavy oxygen water analysis, cupric oxide and Ag_2O should be omitted, and purification confined to several vacuum distillations. Water containing volatile impurities should be given a preliminary purification.

Filling the Float. Air is led into test tube e after distilling the test, in order to fill the float. When this is done, water enters the evacuated float; usually, however, a small bubble of gas remains; to remove this, tube e is turned upside down, by rotating the apparatus in the ground glass joints. On doing this the float will not drop, since it clings to the wall, while the bubble will float up to the open end. By gentle tapping, the water covering the tip of the float flows out, and the apparatus is rapidly evacuated (better still, tap b is opened and closed a few times, while the pump is operating), by turning the apparatus back to its normal position and letting air in. After one or two such operations, the bubble becomes almost invisible; for its final removal, it is dissolved, by compelling it to move in the

Fig. 3. Forceps for manipulating the float.
Fig. 4. Vessel for storing the float.
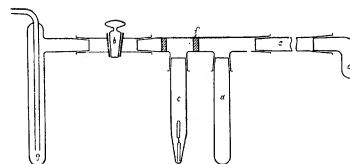
Fig. 5. Apparatus for preparing samples for analysis and for filling the float.

water filling the float (by rocking the apparatus). During this operation care should be taken that the end of the float remains in the water all the time. Before transferring the float into the test tube to be used for analysis, in order to prevent penetration of air into it during the transfer, the float is kept for a few minutes in the apparatus while it is cooled with ice.

Calibration of the Float and Analytical Procedure. The filled float is washed twice on the outside with distilled water at room temperature (held in the platinum hook) and transferred into the test tube used for analysis, containing the same freshly distilled water. Test tube + water are kept in a thermostat all day when analyses are being carried out, otherwise, water saturated in the cold with air, on heating, will give off bubbles which settle on the float and interfere with work*.

The flotation temperature is determined, as in normal flotation methods, by determining the rates of immersion and emersion of the float at several temperatures near to the flotation temperature, constructing appropriate graphs, and interpolating to zero velocity. The simple and reliable thermostat which we used, was developed long ago in our institute [3], and ensured constancy of temperature within 0.001-0.002°.

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* Bubbles can be removed by means of the platinum hook.

Fig. 6. An example of the graph used for determining flotation temperature.

The following example shows how to find coefficient K and carry out the analysis:

It was found that the float filled with water of normal isotope composition (standard) which was purified in our apparatus, moved upwards with a rate of 0.089 of a scale division in 1 second at 27.826°, with a rate of 0.029 division at 27.834°, and a downward rate of 0.173 division in 1 second at 27.873°.

According to these results, as can be seen from Fig. 6, the flotation temperature works out at 27.841°. The flotation temperature, determined in the same way, for a float filled with water with an excess density of $\Delta d = 1277$ *, proved to be 25.779°.

From tables of density for ordinary water we find Δd_{outer} as a difference in densities at 25.779 and 27.841°; $\Delta d_{outer} = 0.996868 - 0.996305 = 563 \gamma$, from which:

$$K = \frac{\Delta d}{\Delta d_{outer}} = \frac{1277}{563} = 2.268.$$

After filling the float with water of unknown excess density Δd_x, a flotation temperature of 26.102° was found, from which $\Delta d_{outer} = 0.996782 - 0.996305 = 447 \gamma$ and $\Delta d_x = 2.268 \cdot 477 = 1082 \gamma$.

As shown experimentally, coefficient K hardly changes at all with time. On the other hand, the flotation temperature of a float filled with standard water, changes somewhat; accordingly we determined it on the day when analyses were made.

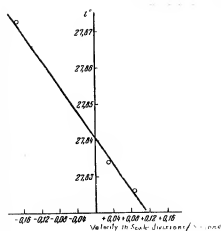The method described has been successfully used over a period of several years in our institute; it ensures an accuracy of 2% on the value determined, as can be seen from the table where a comparison is made of results obtained by means of our method and by the ordinary flotation method respectively, on samples obtained by diluting water of known density.

Sample number	Excess density in γ units		
	Macromethod	Micromethod	Calculated
1	1069, 1067, 1069	(1068)**,1071, 1072	(1068)**
2	754, 753	756, 747	757
3	523, 522	519, 525	526
4	259, 258	254, 254	260

An analysis (including purification of the water) takes 1.5-2 hours.

Evacuation of the Float. The float is evacuated by placing it in tube e (Fig. 5) and the apparatus evacuated. After evaporation of all the water, float and apparatus are ready for a new analysis. During systematic analysis, it is sufficient to wash the apparatus and float with sulfuric acid and permanganate once every 5-10 days.

SUMMARY

A new variant of the micro-flotation method has been suggested for the analysis of heavy and heavy-oxygen water, whereby it is possible to analyze 0.03-0.05 g of water with an accuracy of 2% in the course of 1.5-2 hours.

* The excess density of water used for calibration can be measured accurately by the usual flotation method or by diluting an aliquot of heavy water of known composition.
** Original for calibration and dilution.

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SEPARATION OF NIOBIUM, TANTALUM, AND TITANIUM BY EXTRACTION

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Isolation of niobium, tantalum, and titanium, as well as their separation from other metals of the fourth, fifth, and sixth groups of the Mendeleev Periodic Table which accompany them , is one of the most difficult problems of analytical chemistry.

It is clear from the work of Schoeller, Powell, and Alimarin, et al. [1-6, 17-19], that the use of hydrolysis, and of precipitants such as tannin, salicylic acid, calcium chloride, cinchonine, phenylarsonic acid, and pyrogallol does not lead to a quantitative separation of titanium from elements associated with it.

Werner's research [7], on the separation of niobium, tantalum, and titanium based on the use of differences in the solubility of their ammonium salts in concentrated hydrochloric acid, did not yield reliable results.

Methods for the separation of small amounts of titanium from niobium and tantalum by chromatographic extraction were recently published [8-10]. The methods have their points, but have some essential drawbacks: they are difficult to carry out technically because of the necessity of carrying out work in half-shaded vessels with complex fluoride complexes of niobium, tantalum, titanium, and other elements, and use up to a liter of methylethyl ketone for one analysis; comparative quantitative results for extent of the separation of titanium from niobium and tantalum are not given.

The difficulties of separating titanium from elements which accompany it (niobium, tantalum, and zirconium) are connected with the fact that they do not give normal true solutions; the chemist has to work with complex fluorides or oxalate and tartrate compounds in aqueous solutions; they are not very reactive and do not readily enter into chemical reactions.

Schoeller [1], reasoned that the difficulties of separating niobium, tantalum, titanium, zirconium, tungsten, and certain other elements are connected with "loss of individual properties".

It is known however [11-13], that the individual properties of niobium, tantalum, and titanium, both when they are present simultaneously, or individually, are clearly manifested with respect to polyfunctional phenols having hydroxyl groups in positions 1, 2 or 1, 2, 3 (pyrogallol, pyrocatechol, etc.). Niobium in weakly alkaline solution, or in a neutral oxalate medium gives, with phenols of this type, complex compounds of a yellow color; tantalum forms similar compounds in acid media, while titanium gives a yellow-orange complex compound in acid or alkaline media.

We made it our aim to separate titanium from niobium and tantalum, by extracting their pyrocatechol complex compounds from an oxalate medium at various pH values.

EXPERIMENTAL

A Study of the Conditions for Extracting the Complex Compound of Titanium and Pyrocatechol

During extraction of the titanium-pyrocatechol complex in oxalate solution by certain organic solvents, the complex imparts a yellow-orange color to them.

The changeover of color from one phase to the other does not necessarily indicate extraction of the element. It was essential to study this point experimentally. To do this a standard solution containing 1 mg/ml of titanium (calculated as TiO_2) was prepared. To 500 mg of TiO_2 in a porcelain crucible was added 6-7 g of potassium pyrosulfate and the whole slowly heated till a clear melt of a yellowish color was obtained. The cooled melt was dissolved in hot 3% ammonium oxalate solution, in an amount sufficient to give 500 ml of solution. To 10 ml of the oxalate solution (10 mg TiO_2) was added 10 ml of 3% ammonium oxalate, and at a pH of 3.0 5 g of pyrocatechol

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dissolved in it; after 5-6 minutes, the solution was transferred to a 100 ml separating funnel, and extracted with an equal volume of n-butanol saturated with water. The extract was separated from the aqueous phase, and the butanol evaporated in a porcelain beaker on a water bath; the residue obtained was treated with 20 ml of 10% sulfuric acid, and then, after precipitation with cupferron [14, 16], the titanium was determined either gravimetrically or colorimetrically by the peroxide method [15].

In addition to butanol, the organic solvents listed in Table 1 were tested as potential extractants.

It is clear from Table 1, that titanium is only extracted by polar organic solvents; the highest separation coefficient was achieved with butanol; slightly inferior to this was a mixture of chloroform and butanol, while acetylacetone, ethyl acetate, and methyl butyl ketone were still more inferior in that order.
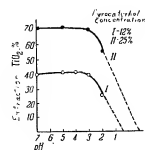

Fig. 1.

It follows therefore from Table 1 that the best extractant for the titanium-pyrocatechol complex is butanol. The distribution coefficient for titanium between the two phases when present in equal amounts, can be increased or decreased by varying experimental conditions, above all by changing the pH of the oxalate solution, and the pyrocatechol concentration respectively (Table 2, Fig. 1).

As is evident from Table 2 and Fig. 1, the optimum conditions for extracting titanium are a pH of the oxalate solution of 7-3, and a pyrocatechol concentration of ~25%; the distribution coefficient of titanium is equal to 2.20-2.40. The distribution coefficient may be increased by increasing the pyrocatechol concentration; when, however, this is done, a homogeneous mass is obtained which it is difficult to separate into phases.

Distribution of titanium between phases when the amount of the phases is varied, is shown in Table 3.

TABLE 1

Distribution of Titanium Between Organic Solvent Phase and Water

Extractant used	Distribution of titanium in %		K*
	in extractant	in water	
Chloroform + n-butanol (1:3)	64.0	36.0	1.78
n-Butanol	70.0	30.0	2.33
Methylsalicylate	0.00	100.0	~
Benzene	0.00	100.0	~
Ethyl ether	0.00	100.0	~
Ligroine	28.0	72.0	~
Methyl butyl ketone	0.00	100.0	0.40
Isoamyl alcohol	31.0	69.0	~
Acetylacetone	24.0	76.0	0.45
Ethyl acetate	0.80	99.2	0.31
Chloroform			0.08

* $\overline{K}$ — distribution coefficient — ratio of titanium concentration in the extractant to that in the aqueous phase.

It is clear from Table 3 that increasing or decreasing the volume of the extractant — butanol — does not affect the phase distribution of titanium. Titanium is distributed between the phases — organic solvent and water in the ratio 70 : 30. Consequently, increasing extractant volume does not give any positive effect.

It is clear from Table 3, that for extraction, one should take a volume of butanol approximately equal to half the volume of the original oxalate solution (aqueous phase). The titanium-pyrocatechol complex probably has a high solubility in butanol, but some of the titanium is not complexed, and cannot transfer to the butanol phase.

The results given in Table 4 were obtained during a study of the relation between titanium distribution and its concentration in the oxalate solution, for an equal volume of the phases, at a pyrocatechol concentration of 20%, and a pH of 3.0.

TABLE 2

Relation Between Titanium Distribution and pH of the Oxalate Solution, and Pyrocatechol Concentration (Original Concentration 0.5 mg/ml TiO_2)

pH	Pyrocatechol concentration in %	Distribution of titanium in %		K
		Butanol	Aqueous phase	
7	12.0	40.2	59.8	0.68
5	12.0	40.0	60.0	0.67
4	12.0	43.2	56.8	0.76
3	12.0	40.4	59.6	0.68
2	12.0	26.0	73.6	0.36
7	25.0	69.0	31.0	2.23
5	25.0	70.4	30.0	2.33
3	25.0	70.8	29.2	2.42
2	25.0	55.2	44.8	1.232

TABLE 4

Distribution of Titanium Between Butanol and Aqueous Phases in Relation to Titanium Concentration

TiO_2 concentration in mg/ml	Distribution of titanium in %		K
	Butanol	Aqueous phase	
0.500	55.12	44.88	1.228
0.333	57.60	42.40	1.358
0.210	62.58	37.42	1.672
0.125	72.00	28.00	2.571

TABLE 3

Distribution of Titanium Between the Butanol and Aqueous Phases in Relation to the Volumes of the Phases (Pyrocatechol Concentration 25%, pH 3)

TiO_2 concentration in mg/ml	Ratio of phases in ml		Distribution of titanium in %	
	Aqueous phase	Butanol	Butanol	Aqueous phase
1	20	10	70.5	29.5
1	10	10	70.3	29.7
0.5	40	20	70.8	29.2
0.5	20	20	69.2	31.8
0.5	12	20	69.0	31.0

It is evident from Table 4 that on decreasing titanium concentration four times, i.e. from 0.5 to 0.125 mg/ml, the distribution coefficient doubles. During extraction, it is expedient to work with less concentrated titanium solutions.

As a result of experimental work, the following optimum conditions for phase distribution of titanium were found: pH 7-3, concentration of pyrocatechol in the oxalate solution 20-25%, a low titanium concentration in solution, and a volume of butanol equal to half of that of the original oxalate solution.

Properties of Metal Pyrocatechinates

In addition to titanium, the following metals form colored complexes with pyrocatechol: iron (III) and (II), uranium (VI), tantalum (V), niobium (V), molybdenum (VI), tungsten (VI) and vanadium (IV). Results on the extraction of the pyrocatechinates of these metals from an oxalate medium are given in Table 5.

TABLE 5

Extraction of Metal Pyrocatechinates from Oxalate Solutions by Butanol

Metal	Extraction of pyrocatechinate		Color	
	pH 2-5	pH 5-8	pH 2-5	pH 5-8
Iron (III)	—	—	—	Blue-violet
Iron (II)	—	—	—	Blue
Uranium (VI)	—	—	—	Brown
Titanium (IV)	+	+	Yellow-orange	Yellow-orange
Niobium (V)	—	+	—	Yellow
Tantalum (V)	+	+	Yellow	—
Molybdenum (VI)	—	—	Yellow-orange	Red
Tungsten (VI)	—	—	Orange	Yellow-green
Vanadium (V)	oxidized	oxidized	Red	Blue

+ extracted
— not extracted

The elements which accompany niobium and tantalum (zirconium, tin, etc.) are not extracted from an oxalate solution; they do not form colored complexes with pyrocatechol, and do not interfere with phase distribution.

It is clear from Table 5, that at pH 5-8, niobium, tantalum, and titanium are extracted, while at pH 2-5, only tantalum and titanium are extracted. Consequently, on this basis, it is possible to separate titanium, tantalum, and niobium from other elements which do not give colored complexes with pyrocatechol, and also from elements, which, in the form of pyrocatechinates are not extracted by butanol (iron, molybdenum, etc). Moreover, it also follows from Table 5, that titanium and tantalum can be separated from niobium in more acid media (pH 2-5). On the basis of the results given in Table 5, it is possible to map out a method of separating the elements: titanium and tantalum are first separated from niobium by using a very acid oxalate medium; subsequently, titanium and tantalum are separated.

Separation of Titanium and Tantalum

The properties of the titanium- and tantalum-pyrocatechol complexes respectively, differ from each other in oxalate solution: the complex with titanium is not stable in a strongly acid medium, the analogous complex with tantalum is,however stable even in a very acid medium. The same is true in butanol solution. Moreover, on treating the extract with acid or alkali solution (Table 5), titanium should be distributed between the aqueous and butanol phases. When this is done, a definite amount of titanium, depending on the given conditions, goes back from the butanol extract during each re-extraction into the aqueous phase.

Re-extraction of titanium from the organic phase increases on using sulfuric acid, and drops off slightly on using hydrochloric acid; other acids proved unsuitable. Distribution of titanium between extract and acid, increases with increasing acidity (Fig. 2).
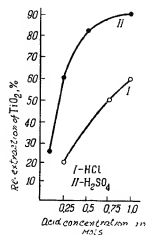

Fig. 2

Fig. 3

Neutral, or weakly alkaline solutions proved less suitable: titanium pyrocatechinate (like the corresponding niobium complex) is more stable in neutral or weakly alkaline media and is difficult to re-extract under such conditions.

Experiments were carried out as follows: in 50 ml lots of oxalate solution, containing tantalum and titanium (0.2 mg/ml of each), at differing pH values /from 1 to 7; the pH was established by means of universal indicator) was dissolved 12 g of pyrocatechol. Solutions were quantitatively transferred from the beakers in which they were made to 100 ml separating funnels, and extraction of the pyrocatechinates of titanium and tantalum was carried out with 25 ml lots of butanol saturated beforehand with water.
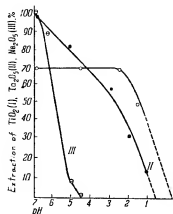
TABLE 6

Separation of Tantalum and Titanium

TiO₂ taken in mg		Found after separation in mg	
Ta₂O₅	TiO₂	Ta₂O₅ : TiO₂	Ta₂O₅	TiO₂
10.00	10.00	1 : 1	10.20	9.8
1.00	10.00	10 : 1	1.08	10.1
0.25	10.00	40 : 1	0.25	9.9
0.50	10.00	20 : 1	0.50	10.1
10.00	10.00	1 : 1	9.90	10.0
5.00	10.00	2 : 1	5.10	10.0
0.20	10.00	50 : 1	0.20	10.1
0.10	10.00	100 : 1	0.08	10.1
1.00	10.00	10 : 1	0.95	9.9
2.00	10.00	5 : 1	2.00	10.0

In order to separate the titanium-pyrocatechol complex, the extract containing tantalum and titanium was treated in a separating funnel a few times with 5% sulfuric acid. During the last extraction, the aqueous phase should be colorless or have a pale-yellow color, which indicates practically complete removal of titanium (aqueous phase) from the tantalum (extract). The extract was evaporated on a water bath and to the residue was added 15-20 ml of water; the whole was then evaporated again almost to dryness; the residue was finally dissolved in 30 ml of 10% sulfuric acid by heating; after cooling, 8-10 ml of cupferron solution was added. The residue was filtered off, transferred to a crucible, dried, calcined, and the residue fused with the least possible amount of potassium pyrosulfate. The cooled melt was dissolved by heating in 25-50 ml of ammonium oxalate. The oxalate solution was adjusted to a pH of 7-8 by means of a sodium sulfate solution. ~ 5% of pyrocatechol dissolved in it, and the whole transferred to a separating funnel; tantalum pyrocatechinate was extracted once with half the volume of solution of butanol. The extract was treated 2-3 times with 5% sulfuric acid, and, as indicated above, the tantalum was transferred into an oxalate solution – 10 ml – (or any other necessary volume); tantalum was then determined colorimetrically by the pyrogallol method, or gravimetrically after precipitation with cupferron [14].

Titanium (after removal from tantalum) was determined gravimetrically by the cupferron method [14, 16].

Experiments showed that ~ 70% of the titanium can be extracted by one treatment at a pH of 3.0-7.0 (Fig. 3, Curve 1), while extraction of tantalum increases with increasing pH of the oxalate solution (Fig. 3, Curve II); at a pH of 7, extraction of tantalum is 100%.

Table 6 gives the results of separation of tantalum and titanium from an oxalate solution (50 ml) under the following conditions: pH 3, concentration of pyrocatechol during repeated extractions – 20%, a volume of butanol half the volume of oxalate solution to be extracted. Four extractions of tantalum and titanium are necessary for quantitative separation. Subsequent procedure was the same as that described above.

It is clear from Table 6, by using the method described, that it is possible to separate these elements quantitatively, even for ratios of TiO₂ : Ta₂O₅ of 100 : 1. It is particularly difficult to separate traces of titanium (< 100 γ) from tantalum. On repeated extraction at pH 7 however, it is possible to remove even such small amounts as these from tantalum.

Phase Distribution of Niobium with Respect to pH of the Oxalate Solution

Niobium forms a complex with pyrocatechol in neutral or weakly alkaline media (Table 5). At a pyrocatechol concentration of ~ 5%, niobium goes over quantitatively from an oxalate medium into the butanol in the form of a yellow niobium-pyrocatechol complex.

Tests were carried out as follows: to 50 ml of an oxalate solution of niobium (0.2 mg/ml), at pH values ranging from 3 to 7, was added 2.5 g of pyrocatechol. After the latter had dissolved, the solution was transferred to a separating funnel and extracted once with half its volume of butanol. The extract was separated from the aqueous phase, butanol removal by evaporation, and the residue dissolved in 25 ml of dilute sulfuric acid; niobium was finally determined either gravimetrically with cupferron, or colorimetrically by the pyrogallol method [11, 14].

It was established in this way that niobium, as the pyrocatechinate,is transferred quantitatively into butanol at a pH of 7 (Fig. 3, Curve III); it starts to be extracted at a pH of 4.5. It is clear from Fig. 3 that niobium, tantalum, and titanium, have a different phase distribution.

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At a pH of 7, 100% of the niobium and tantalum pass over from the aqueous phase into butanol, while only 70% of the titanium passes over. in each case for a pyrocatechol concentration of 25%; on lowering pyro-catechol concentration to 6-12% extraction of titanium drops to 40% (Table 2).

A Method for Separating Niobium, Tantalum, and Titanium

As a result of preliminary work the following analytical procedure was adopted: a mixture of the oxides of niobium, tantalum, and titanium, in amounts of up to 20-22 mg, was fused with ∼ 1 g of potassium pyro-sulfate; the cooled melt was dissolved by heating in 25-50 ml of 3% ammonium oxalate, and sodium sulfate or dilute sulfuric acid added dropwise to the solution until the pH was 3 (using Tropeoline 00 as indicator); pyrocatechol was then added in an amount equal to ∼ 20% of the original solution. The solution was transferred to a separating funnel and repeatedly extracted with half its volume of butanol, pyrocatechol being added each time.

After 4-5 extractions, the oxalate solution became almost colorless, indicating quantitative removal of titanium. The last extraction with butanol was carried out without addition of pyrocatechol. After extractive separation of titanium and tantalum, the oxalate solution, containing niobium, was transferred from the funnel to a flask and a colorimetric or gravimetric determination carried out [11, 14].

TABLE 7

Separation of Niobium, Tantalum, and Titanium

Taken in mg				Found in mg		Error in %	
TiO_2	Nb_2O_5	Ta_2O_5	$\frac{TiO_2}{Me_2O_5}$	Ta_2O_5	Nb_2O_5	Ta_2O_5	Nb_2O_5
10,00	1,00	1,00	5 : 1	0,95	1,08	— 5,0	+ 8,0
10,00	10,00	0,30	1 : 1	0,33	9,60	+10,0	— 4,0
10,00	10,00	0,20	1 : 1	0,20	9,70	0,0	— 3,0
10,00	0,50	0,50	10 : 1	0,50	0,52	0,0	+ 4,0
10,00	5,00	1,00	5 : 3	1,04	4,88	+ 4,0	— 2,5
10,00	10,00	0,50	1 : 1	0,53	9,72	+ 6,0	— 2,8
10,00	15,00	0,25	1 : 1,5	0,30	15,40	—12,0	+ 2,6
20,00	0,40	0,30	30 : 1	0,33	0,44	+10,0	+10,0
20,00	0,20	0,20	50 : 1	0,20	0,20	0,0	0,0
—	5,00	0,10	—	0,09	4,80	—10,0	— 4,0
—	10,00	0,10	—	0,09	9,80	—10,0	—4,0

The extract (first two combined extracts), containing tantalum and titanium, was treated in a separating funnel a few times with 5% sulfuric or hydrochloric acid in order to remove the titanium. During the last re-extraction the solution should be colorless or have a weak yellow color, indicating an almost complete removal of titanium (aqueous phase) from tantalum (extract). The extract (after removal of the aqueous phase) was evaporated on a water bath, and to the residue was added 15-20 ml of water and the whole re-evaporated; the residue was dissolved on heating in 20-25 ml of 8-10% sulfuric acid (for quantities of tantalum: < 1 mg, 1 mg of a 1% salt solution was added as collector) and after cooling 8-10 ml of 3% cupferron solution. The cupferronates were filtered off, transferred to a crucible, dried, and calcined, and the residue fused with as little as possible of potassium pyrosulfate. The cooled melt was dissolved on heating in 20 ml of 3% ammonium oxalate. After dissolving ∼ 5% of pyrocatechol in it, the oxalate solution was adjusted to a pH of 7-8 by means of sodium sulfate, transferred to a separating funnel and the tantalum pyrocatechinate extracted once with 8-10 ml butanol. The extract was treated 2-3 times with 5% sulfuric acid, and then evaporated, and, as indicated above, the tantalum was transferred to an oxalate solution — 10 ml — or the requisite volume, and colorimetric determination of tantalum carried out [11, 14].

Results on the separation of niobium, tantalum, and titanium, are given in Table 7.

It is clear from Table 7 that niobium, tantalum, and titanium can be quantitatively separated with not too great an error of up to ± 10%. It is also possible, again as shown in Table 7, to separate two elements i.e. niobium and tantalum.

In conclusion we should point out that niobium, tantalum, and titanium form complexes with all poly-functional phenols having hydroxyl groups in the 1, 2 or 1, 2, 3 positions, but not all the compounds of these elements with the phenols are extracted. It is easier to extract the pyrocatechinates than the pyrogallates. Niobium, tantalum, and titanium cannot be extracted at all in the form of their compounds with protocatechuic aldehyde or protocatechuic acid respectively.

Carboxyl, aldehyde, and sulfonate groups in the phenol molecule prevent solution of the complex in the extractant, though these phenols themselves, containing these same groups, are more readily soluble in water, than e.g. in butanol. The same is true of the analogous derivatives of pyrogallol and alizarine. The high solubility of the reagent-complexing agent in the extractant favors the transfer of the element from the aqueous phase to the organic phase. The reagent-complexing agent goes over from the aqueous phase into the organic phase together with niobium, tantalum, or titanium.

When the properties of the phenol, containing hydrophilic (sulfonate group, carboxylic, etc) groups, are closer to water than to the extractant, and if the complexing agent itself is incapable of going over from the aqueous phase to the organic one, then only the color of the complex can be observed, but not its extraction.

During our work we payed attention to the concentration of the pyrocatechol during extractive distribution of the elements, particularly titanium. At high concentrations of pyrocatechol in oxalate solution (20-25%) the properties of titanium with respect to the aqueous phase are not manifested separately: pyrocatechol is extracted together with titanium, since it is more soluble in butanol than in water. Such phenomena are observed e.g. when calcium, as the stearate, is readily extracted by an organic solvent; while in true solutions of calcium, this process is not observed. The chemical nature of the solvent is of significance. Pyrocatechol is sparingly soluble in chloroform or benzene, and metal pyrocatechinates do not pass over into these extractants.

No relationship was observed between pyrocatechol concentration and tantalum during phase distribution. Even at pyrocatechol concentrations of 0.25%, tantalum quantitatively passed over into butanol from an oxalate solution at a pH of 7.

Tantalum passes over as the pyrocatechinate from the aqueous phase into the organic one at a concentration of 0.5 mg/ml. Niobium, at the same concentration, quantitatively passes into the butanol as the pyrocatechinate at concentrations of pyrocatechol in the oxalate solution of more than 3%. Niobium passes over into the butanol considerably more readily than titanium, but not so readily as tantalum. The changeover into the organic phase, is probably determined by differences in stability of the oxalate complexes. The stability of the oxalate complexes can be arranged as follows: Ti > Nb > Ta. Quantitative transfer of the pyrocatechinates into the organic phase may be arranged in the following order: Ta < Nb < Ti.

During re-extraction the reverse phenomenon is observed: titanium passes into the aqueous phase more readily than tantalum. Only hydrogen fluoride will effect a transfer of tantalum into the aqueous phase.

SUMMARY

1. Niobium, tantalum, and titanium, as the pyrocatechinates, depending on the pH of the oxalate solution, can be extracted with n-butanol.

The phase distribution of the pyrocatechinates of niobium, tantalum, and titanium has been studied under various conditions, and, on this basis, a method is suggested for the quantitative separation of these elements. The method in essence depends on the fact that titanium and tantalum can be separated from niobium at a pH of 3. Titanium and tantalum are separated by re-extraction with 5% sulfuric acid, followed by repeated extraction of the tantalum pyrocatechinate for a low pyrocatechol content. The method gives experimental errors of the order of ± 10%.

2. It has been established that only niobium, tantalum, and titanium can be extracted as their pyrocatechinates, for a definite phase distribution for each element; other elements (iron, zirconium, tin etc.) are not extracted, and do not affect phase distribution.

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SEPARATION OF MAGNESIUM, ALUMINUM, CHROMIUM, MANGANESE, IRON NICKEL, AND COPPER BY AN ION-EXCHANGE METHOD

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Numerous investigations have been devoted to the application of ion-exchange chromatography in analytical chemistry for the selective separation of a component which it is desired to determine. The literature on this problem includes review articles symposiums and monographs which have appeared recently [1-8]. In works published earlier [8-13], the advantages of the ion-exchange method over the chemical methods normally employed for separation have been demonstrated.

In the present article we have given a number of examples of separation of metals during analysis of alloys, in which the synthetic cation-exchange resin KU-2 was employed.

Separation of Copper from Aluminum. During analysis of bronzes containing aluminum, copper is deposited electrolytically on a mercury cathode. It is simpler to separate these methods by means of a cation-exchange resin.

One of the methods for separating copper and aluminum by means of a cation-exchange resin is based on the capacity of copper to give a complex compound with thiosulfate [14], according to the equation:

$$2CuSO_4 + 6Na_2S_2O_3 \longrightarrow 2Na_3[Cu(S_2O_3)_2] + Na_2S_4O_6 + 2Na_2SO_4.$$
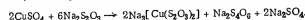
On addition of sodium thiosulfate to a solution of copper and aluminum salts, until the solution is decolorized, copper is converted into the complex anion $[Cu(S_2O_3)]^{3-}$, while aluminum remains unchanged as Al^{3+}. The solution treated in this way is passed through a column filled with a cation-exchange resin in the Na-form; the active groups of the resin only hold back aluminum ions. Copper as the complex thiosulfate anion passes through into the filtrate. When this method is used, the cation-exchange resin cannot be employed in the H-form, since acid would be formed in the column which would break down the anion $[Cu(S_2O_3)]^{3-}$, and the copper would also be absorbed by the resin. The filtrate plus washings are acidified with HCl and boiled until the solution is perfectly clear. The precipitate of copper sulfide formed is dissolved and copper determined iodometrically. Aluminum is eluted from the column with 4N HCl. It is determined in the eluate by the hydroquinoline method.

Results for separation of copper from aluminum in synthetic mixtures are given in Table 1.

As is evident from the results, satisfactory separation of copper from aluminum is achieved. Another method of separating copper and aluminum is based on making use of the amphotericity of aluminum, and the formation of ammines. Addition of ammonia to a solution containing copper and aluminum, leads to the formation of the ammine $[Cu(NH_3)_4]$ $(NO_3)_2$. Aluminum, however, is precipitated as the hydroxide. On addition of sodium hydroxide to this intensely blue-colored solution + precipitate, the precipitate of $Al(OH)_3$ dissolves to form the aluminate $NaAlO_2$. In the final solution which has been formed as the result of this successive treatment with ammonia and sodium hydroxide respectively, the copper and aluminum are in solution in the form of complex ions of opposite charge: $[Cu(NH_3)_4]^{2+}$ and $[AlO_2]^{-}$.

TABLE 1

Taken in g		Found, after separation, in g	
Cu	Al	Cu	Al
0.0300	0.0300	0.0305; 0.0295; 0.0290	0.0320; 0.0298; 0.0320
0.0600	0.0100	0.0600; 0.0620; 0.0590	0.0101; 0.0109; 0.0098

The cation-exchange resin must be in the Na-form for separation of these ions. If the resin is used in the H- or ammonium form, then the aluminate, on passing through the column will be converted back into the hydroxide which will be held up between the particles of resin. Aluminum will, accordingly, not be found in the filtrate.

On passing a solution of the salts of copper and aluminum, treated successively with ammonia and alkali, through a column of the resin in the Na-form, copper as the ammine will be absorbed by the active groups of the resin:

$$2RSO_3Na + [Cu(NH_3)_4]^{2+} \rightarrow (RSO_3)_2[Cu(NH_3)_4] + 2Na^+.$$
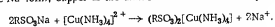
The aluminate will pass through such a column into the filtrate. The filtrate containing the aluminate, together with wash water is neutralized with acetic acid and aluminum determined as indicated already by the hydroxyquinoline method.

Copper is eluted from the column with 4N HCl. As a result of this treatment, the resin is regenerated:

$$(RSO_3)_2[Cu(NH_3)_4] + 6HCl \rightarrow 2RSO_3H + CuAl_2 + 4NH_4Cl.$$
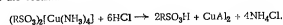
Copper is determined in the filtrate iodometrically. After removal of copper, the resin will be in the H-form. In order to convert the resin back into the Na-form, a 5% solution of NaOH is passed through the column; the column is finally washed with distilled water to a neutral reaction. Results for separation of copper from aluminum by this method are given in Table 2.

TABLE 2

Taken in g		Found, after separation, in g	
Cu	Al	Cu	Al
0.0300	0.0300	0.0290; 0.0310; 0.0300	0.0290; 0.0300; 0.0310
0.0300	0.0100	0.0320; 0.0300; 0.0298	0.0110; 0.0095; 0.0090
0.0100	0.0300	0.0095; 0.0110; 0.0100	0.0285; 0.0310; 0.0290

Separation of copper from aluminum by this method gives satisfactory results also.

Separation of Copper, Aluminum, and Magnesium. Initially it was suggested that copper, aluminum, and magnesium could be separated on the basis of the interaction of the mixture of salts in solution with ammonia and alkali. In this case, however, magnesium will be precipitated as the hydroxide. Dissolving the $Mg(OH)_2$ in the presence of ammonium chloride did not give good results either. On passing such a solution, containing excess ammonium chloride, through a column of cation-exchange resin in the Na-form, aluminum is also precipitated as the hydroxide, as the result of hydrolysis. Accordingly, in order to remove copper, test solution was treated with thiosulfate till it was colorless. On passing such a solution through a column in the Na-form, copper as the ion $[Cu(S_2O_3)_2]^{3-}$ passed through into the filtrate and was determined as usual.

The active groups of the resin, in addition to the aluminum, also absorb magnesium:

$$2RSO_3Na + Mg^{2+} \rightarrow (RSO_3)_2Mg + 2Na^+.$$
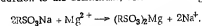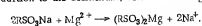
To separate the magnesium and aluminum absorbed on the column, use is made of the amphotericity of the latter. In this case a solution of 5% alkali was used for washing the aluminum ions off the column:

$$(RSO_3)_3Al + 4NaOH \rightarrow 3RSO_3Na + Na\,AlO_2 + 2H_2O.$$
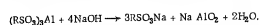
Aluminum was determined in the filtrate by the usual method. Alkali washing of the column does not lead to removal of the magnesium held by the active groups of the resin; this can only be affected by washing the column, after alkali treatment, with 4N HCl.

$$(RSO_3)_2Mg + 2HCl \rightarrow 2RSO_3H + MgCl_2.$$

TABLE 3
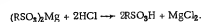
Ratio Cu : Al : Mg	Taken in g			Found, after separation, in g		
	Cu	Al	Mg	Cu	Al	Mg
1:1:1	0.0300	0.0300	0.0300	0.0300; 0.0294; 0.0295	0.0300; 0.0300; 0.0295	0.0300; 0.0310; 0.0300
1:1:1	0.0600	0.0300	0.0300	0.0600; 0.0620; 0.0320	0.0320; 0.0300; 0.0630	0.0300; 0.0310; 0.0310
2:1:1	0.0600	0.0300	0.0300	0.0600; 0.0285; 0.0320	0.0585; 0.0610; 0.0300	0.0285; 0.0300; 0.0300
1:1:2	0.0300	0.0300	0.0600	0.0300; 0.0285; 0.0300	0.0277; 0.0290; 0.0300	0.0630; 0.0600; 0.0600
2:1:2	0.0600	0.0300	0.0600	0.0620; 0.0610; 0.0600	0.0600; 0.0300; 0.0300	0.0300; 0.0610; 0.0600
2:2:1	0.0600	0.0600	0.0300	0.0300; 0.0290; 0.0320	0.0290; 0.0300; 0.0600	0.0290; 0.0000; 0.0010
2:2:2	0.0600	0.0600	0.0600	0.0290; 0.0285; 0.0300	0.0578; 0.0600; 0.0579	0.0610; 0.0600; 0.0600

* Satisfactory results were also obtained in this rather more complicated mixture.

TABLE 4

Ratio Fe : Cr	Taken, in g		Found, after separation, in g	
	Fe	Cr	Fe	Cr
1:1	0.0100	0.0100	0.0100	0.0101
2:1	0.0100	0.0050	0.0110	0.0050
1:2	0.0050	0.0100	0.0050	0.0100
4:1	0.0400	0.0100	0.0410	0.0120
1:4	0.0100	0.0400	0.0100	0.0390

Magnesium was determined in the filtrate by the hydroxyquinoline method. Results for the separation of copper, aluminum, and magnesium are given in Table 3.
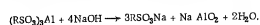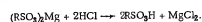
Separation of Chromium from Iron. For separation of chromium from iron, use was made of the difference in stability of their thiocyanate complexes. On heating a solution of a chromium salt with ammonium thiocyanate, a stable complex is formed.

$$CrCl_3 + 6NH_4SCN \rightarrow (NH_4)_3[Cr(SCN)_6] + 3NH_4Cl.$$
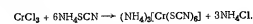
The complex formed between iron and thiocyanate under the same conditions is very unstable.

Passage of the intensely colored solution formed, containing these metals, through a column in the H-form leads to their separation. Chromium as the complex anion with the composition $[Cr(SCN)_6]^{3-}$ readily passes into the filtrate. On heating the filtrate with nitric acid, the complex chromium compound is decomposed; after treatment with sulfuric acid chromium is determined by the persulfate-silver method.

The iron in the solution being analyzed is absorbed by the active groups of the resin:

$$3RSO_3H + Fe^{3+} \rightarrow (RSO_3)_3Fe + 3H^+.$$
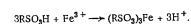
After removal of chromium as the complex anion, iron is eluted from the column with 4 N HCl. After washing the column until there is no longer any reaction for iron (thiocyanate test), iron is determined in the second filtrate + washings, by one of the usual methods.

Results for separation of this pair of elements are given in Table 4.

Chromium and iron can also be separated by another method. As indicated above, chromium gives a complex compound with thiocyanate, which is considerably more stable than the iron one. With pyrophosphate, the reverse holds true.

The pyrophosphate complex of iron is formed according to the equation:

$$2FeCl_3 + 3Na_4P_2O_7 \rightarrow Na_6Fe_2(P_2O_7)_3 + 6NaCl;$$
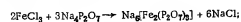
the complex thus formed, is so stable, that the complex anion $[Fe_2(P_2O_7)_3]^{6-}$ still exists at a pH of 1. It is interesting to note

that the anionic form of iron is maintained also at very high pH values of 10-11, when ammonia is added to the original solution. Under these conditions, there is a sharp change in the color of the solution from yellow to red, which is, presumably, connected with a transformation into the inner sphere of the complex according to the reaction:

$$Na_2[Fe_2(P_2O_7)_3] + 4NH_4OH \rightarrow 2Na[FeP_2O_7(NH_3)_2] + Na_4P_2O_7 + 4H_2O.$$
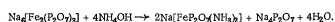
The complex formed between chromium and pyrophosphate breaks down completely at a pH of 3, to form the simple chromium cation.

As a result of experimentally chosen conditions, a mixture of iron and chromium can be separated quite well, if the solution acidified to a pH of 1-3 contains pyrophosphate in amounts no less than in the ratio $Me^{3+} : P_2O_7^{4-} = 1 : 4$. Test solution prepared in this way will contain the two metals in the form of ions of opposite charge: $[Fe_2(P_2O_7)_3]^{6-}$ and Cr^{3+}. On passing such a solution, containing oppositely charged ions, through a column in the Na-form, iron will pass into the filtrate, while chromium will be held by the active groups of the resin:

$$3RSO_3Na + Cr^{3+} \rightarrow (RSO_3)_3Cr + 3Na^+.$$
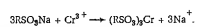
Iron is separated from the filtrate by boiling it with alkali and is then determined by one of the usual methods. Removal of chromium from the column is effected by eluting the latter with 10% H_2SO_4:

$$2(RSO_3)_3Cr + 2H_2SO_4 \rightarrow 6RSO_3H + Cr_2(SO_4)_3.$$
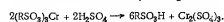
Chromium is determined in the second filtrate by the same method. Results for the separation of chromium and iron by the pyrophosphate method are given in Table 5.

These results demonstrate that, in this case, chromium and iron are separated satisfactorily.

TABLE 5

Ratio Fe : Cr	Taken in g		Found, after separation, in g	
	Fe	Cr	Fe	Cr
1 : 1	0.0100; 0.0100		0.0100; 0.0102	0.0103; 0.0101
1 : 2	0.0050; 0.0100		0.0051; 0.0050	0.0100; 0.0101
2 : 1	0.0100; 0.0050		0.0107; 0.0103	0.0050; 0.0053
1 : 10	0.0050; 0.0500		0.0051; 0.0050	0.0511; 0.0515
10 : 1	0.0500; 0.0050		0.0503; 0.0512	0.0052; 0.0050

Separation of Manganese from Iron. Manganese can be readily separated from iron, as in the previous instance, by using sodium pyrophosphate as complexing agent. On acidifying the interacting solutions to a pH of 2-3, only iron forms a complex anion. On passing the solution through a column in the Na-form, manganese under these conditions will be held by the active groups of the resin:

$$2RSO_3H + Mn^{2+} \rightarrow (RSO_3)_2Mn + 2H^+.$$
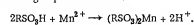
Iron passes into the filtrate. After breakdown of the complex, iron is determined as usual.

Manganese is washed off the resin with 10% H_2SO_4.

$$(RSO_3)_2Mn + H_2SO_4 \rightarrow 2RSO_3H + MnSO_4.$$
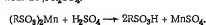
Manganese is determined in the filtrate by one of the usual methods. Results for the separation of iron and manganese are given in Table 6.

Separation of Chromium from Manganese. On the basis that chromium alone forms a complex anion $[Cr(SCN)_6]^{3-}$ with thiocyanate, while manganese remains as the simple cation Mn^{2+}, these two metals can be readily separated from each other by means of a column of resin in the Na-form. The practical procedure for separating this pair of elements is the same as that described for the separation of iron from chromium. Results for the separation of a mixture of manganese and chromium are given in Table 7.

TABLE 6

| Taken in g		Found, after separation, in g	
Fe	Mn	Fe	Mn
0.0400	0.0200	0.0381; 0.0410; 0.0427	0.0179; 0.0190; 0.0219

Separation of manganese and chromium is also possible on the basis of formation of a stable complex compound between chromium and pyrophosphate. An oily liquid with a dark green color separates out from a solution of chromium plus pyrophosphate on addition of a mixture of alcohol and ether. On drying in a desiccator over concentrated sulfuric acid, this oily liquid crystallizes. According to analytical results, the composition of the material formed corresponds to the formula: $Na_3[CrP_2O_7]_2]H_2O$. Thus, chromium on interacting with pyrophosphate (on heating) in solution appears in the form of a complex anion: $[CrP_2O_7)_2]^{3-}$, while manganese under the same conditions, is found in the form of the simple Mn^{2+} cation. On passing a mixture of the ions of these metals through a column filled with a cation-exchange resin in the Na-form, only chromium passes through into the filtrate, while manganese is absorbed by the active groups of the resin. First chromium, and then, after washing off the column, manganese, are determined in the filtrates separately, by the usual methods. Results for separation of manganese and chromium on the basis of a pyrophosphate treatment are given in Table 8.

TABLE 7

Taken in g		Found, after separation, in g	
Mn	Cr	Mn	Cr
0.0100	0.0090	0.0100; 0.0110; 0.0100	0.0093; 0.0098; 0.0089

TABLE 8

Taken in g		Found, after separation, in g	
Mn	Cr	Mn	Cr
0.010	0.0090	0.0120; 0.0130; 0.0100	0.0097; 0.0089; 0.0094
0.010	0.0100	0.0110; 0.0120; 0.0110	0.0090; 0.011 ; 0.010

TABLE 9

Taken in g			Found, after separation, in g		
Fe	Cr	Mn	Fe	Cr	Mn
0.030	0.009	0.010	0.031; 0.031; 0.028	0.0087; 0.0093; 0.0113	0.0133; 0.0131; 0.0149

Separation of Iron, Chromium, and Manganese. On the basis of the reactions described above, separation of mixtures consisting of iron, chromium, and manganese, can be effected by various methods. Possibly, a more effective variant is that in which use is made of the capacity of iron to give a stable complex compound with

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pyrophosphate at low pH values. In this case, iron as the negative complex anion $[Fe_2(P_2O_7)_3]^{4-}$, passes into the filtrate, while chromium and manganese (Cr^{3+}, Mn^{2+}) are absorbed by the active groups of the resin. After removal of chromium and manganese from the column, they are separated from each other by converting the chromium into the thiocyanate complex. On repeated passage of the solution through a column in the Na-form, chromium passes into the filtrate as the anion $[Cr(SCN)_6]^{3-}$, in which it is determined. The manganese absorbed by the column is eluted by means of 10% sulfuric acid.

Table 9 contains the results on separation of a mixture consisting of iron, chromium, and manganese.

Separation of Chromium and Nickel. During analysis of steel, separation of this pair of metals by means of ion-exchange chromatography is also simple. In this case again, it is possible to make use of the capacity of chromium to form a stable complex with thiocyanate, while nickel remains as the divalent cation under these conditions. On passing a mixture of the dissolved metals through a column containing a cation-exchange resin in the Na-form, nickel is absorbed by the active groups of the resin:

$$2RSO_3Na + Ni^{2+} \longrightarrow (RSO_3)_2Ni + 2Na^+.$$
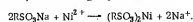
Chromium passes into the filtrate as $[Cr(SCN)_6]^{3-}$. Nickel is eluted from the column with 4 N HCl. Nickel is determined by one of the usual methods.

Results for the separation of chromium and nickel are given in Table 10.

TABLE 10

Taken in g		Found, after separation, in g	
Cr	Ni	Cr	Ni
0.0500	0.1500	0.0477; 0.0496; 0.0490	0.1462; 0.1510; 0.1490

Examples are given below of the chromatographic separation of metals in production samples.

1. Determination of Chromium. 0.05 g of ferro-chrome is dissolved in 30 ml of H_2SO_4 (1:2) by heating on a sand bath. 5 ml of HNO_3 is added and the mixture heated till white fumes of sulfuric acid appear. Metals are precipitated by ammonia as hydroxides; the precipitates are filtered off and dissolved in hydrochloric acid. The solution of chlorides is evaporated to dryness, the dry residue is dissolved in water, and, after addition of 10 ml of 5% NH_4SCN, the whole is evaporated to dryness again. The final residue is dissolved in a small amount of water, and the solution passed through a column in which the resin (20 g) is in the H-form; the column is washed with distilled water.

Filtrate plus wash water containing the thiocyanate complex of chromium is used for the quantitative determination of chromium. Iron is not determined quantitatively. To the filtrate containing chromium 1-2 ml of HNO_3 is added to destroy the complex. 20 ml of H_2SO_4 is added to the solution which is then evaporated to the appearance of sulfuric fumes, after which chromium is determined by the persulfate-silver method. In our sample we found 59.60, 59.30, and 59.45% Cr.

Using the same method, chromium was determined in a standard sample N 167, containing 74.60% Ni and 21.1% Cr. In this alloy we found 20.99, 21.38 and 21.18% Cr.

2. Determination of Iron. 0.1 g of ferro-manganese is dissolved in 50 ml of HCl by warming, 1-2 ml of hydrogen peroxide is added to the solution to oxidize divalent iron; it is then evaporated to dryness and the dry residue dissolved in 15-20 ml of water. 25 ml of 10% sodium pyrophosphate (pH 3) is added to convert iron into the complex anionic form. The solution obtained is passed through a column with a cation-exchange resin in the Na-form. NaOH is added to the filtrate plus wash liquor and the whole boiled for destroying the iron pyrophosphate complex. Ferric hydroxide is filtered off and after repeated reprecipitation, the iron determined gravimetrically. In our test sample we found 34.63, 35.00, and 34.56% Fe.

SUMMARY

By applying ion exchange chromatographic methods it is possible to separate various metals from their mixtures, with their subsequent determination, more easily than by other methods.

Copper can be separated from aluminum by converting these elements into ions of different charge. On interaction with thiosulfate, only copper forms a complex anion $[Cu(S_2O_3)_2]^{3-}$; while in ammoniacal media, these metals are transformed respectively into various types of complex ions: $[Cu(NH_3)_4]^{2+}$ and $[AlO_2]^{-}$. This technique can be used for separating mixtures of copper, aluminum, and magnesium. In this case, after removal of copper and aluminum as complex anions, magnesium, which remains on the resin in the column, is determined by the usual method after desorption with acid.

Separation of chromium from iron is possible on the basis that in the presence of thiocyanates, only chromium forms a stable complex anion $[Cr(SCN)_6]^{3-}$; iron remains as the simple cation and is absorbed by the active groups of the resin. During interaction of these metals with pyrophosphates, the opposite is true. In this case, iron forms a complex anion $[Fe_2(P_2O_7)_3]^{4-}$; chromium remains as the simple cation.

The reaction with pyrophosphate can also be used for separating iron from manganese. Reaction with thiocyanate is more convenient for separating chromium from manganese. Using the techniques described, it is also possible to separate chromium from nickel, and to separate ternary and quaternary mixtures of the metals listed above.

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* T. p. = C. B. Translation pagination.

COLORIMETRIC DETERMINATION OF TRACES OF COPPER IN METALLIC NICKEL
AND ITS COMPOUNDS IN THE ULTRA-VIOLET

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At present, despite the large number of methods for the colorimetric determination of copper [1], there is no satisfactory method for determining traces of copper in nickel, its alloys, and salts. In most methods it is essential to carry out a preliminary separation of copper from elements accompanying it, in particular from nickel and cobalt.
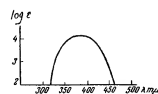
Fig. 1. Absorption curve for the ammonia-bromide complex of copper.
mea

In order to solve this problem, we made use of the capacity of univalent copper to give a complex compound with ammonia, which has a high absorption coefficient in the ultra-violet. The analogous compound of nickel exhibits only a weak absorption in this region. Copper was reduced with ascorbic acid in the presence of potassium bromide. The work was carried out on an ultra-violet photometer [2]. Quartz cuvettes of 3 and 2.5 cm thickness were used.

In order to decide at which wave length, colorimetric measurements should be carried out, the character of the absorption of ultra-violet light by the ammonia complex of univalent copper in the wave length range 450 to 300 mμ was studied on a Russian SF-11 spectrophotometer. The absorption curve shown in Fig. 1 was obtained. It is clear from this curve, that the optimum wave length range at which colorimetric measurements can be carried out is that extending from 360-400 mμ.

TABLE 1

Introduced		Cu : Ni	Found	Error	Introduced		Cu : Ni	Found	Error
Cu γ/ml	Ni γ/ml		Cu γ/ml	γ/ml	Cu γ/ml	Ni γ/ml		Cu γ/ml	γ/ml
0,55	800	1 : 1455	0,55	0,00	2,21	1000	1 : 453	2,30	+0,09
0,55	1050	1 : 1910	0,50	−0,05	2,21	1550	1 : 701	2,10	−0,11
0,92	50	1 : 54	0,90	−0,02	3,70	1000	1 : 270	3,70	0,00
0,92	500	1 : 543	0,90	−0,02	3,70	1550	1 : 419	3,60	−0,10
0,92	1050	1 : 1143	0,92	0,00	11,07	1050	1 : 95	11,10	+0,03
1,48	1000	1 : 676	1,45	−0,03	11,07	1550	1 : 140	11,15	+0,08
1,48	1500	1 : 1014	1,70	+0,22					

Experiments carried out in order to study the stability of the ammonia complex, showed that the highest optical density corresponding to maximum absorption by the complex, is observed on adding 25 ml of ammonia

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solution (1:1) to the test solution. The "color" of the complex attains its maximum density after 30 minutes, and does not change in the course of 20 minutes.

Construction of a Calibration Curve

After choosing the conditions for carrying out colorimetric measurements, we carried out tests to find out whether or not solutions containing the ammonia complex of univalent copper obey Beer's law, and constructed a calibration curve.

In view of the fact that the working solution of the mixture of reagents exhibits light absorption, colorimetric measurements were carried out with respect to a reference solution; to this solution was added 2 ml of a 1% solution of ascorbic acid, 2 ml of a saturated solution of potassium bromide, and 25 ml of ammonia solution (1:1), and the total volume made up to 50 ml with distilled water. Optical densities were measured 30 minutes after addition of ammonia.
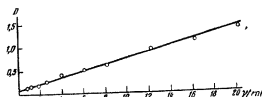
Fig. 2. Calibration Curve.

The shape of the curve, obtained by measurements of a series of solutions containing traces of copper, is shown in Fig. 2. It is evident from this curve that in the concentration range for copper of 0.5 γ/ml to 20 γ/ml a straight line proportionality can be observed between copper concentration and optical density of solution. Within this concentration range therefore, it is possible to carry out colorimetric determination of copper by measuring the absorption of its ammonia complex in the wave-length range $\lambda = 365-380$ mμ.

Determination of Copper in the Presence of Large Amounts of Nickel

To determine copper in the presence of nickel we prepared synthetic solution containing small amounts of copper and large amounts of nickel. The amount of copper was determined by means of the calibration curve constructed previously.

As pointed out, the ammonia complex of nickel also exhibits absorption of the ultra-violet in the region 360-380 λ, but this absorption is insignificant. Nevertheless, in order to inhibit this effect of nickel, a similar amount of nickel was added to the reference solution to that contained in test solutions. Using such a technique, nickel does not interfere with copper determination, as can be seen from the results obtained (Table 1), for ratios of Cu:Ni = 1:1500.

As can be seen from the results obtained, experimental error for ratios of Cu:Ni ranging from 1:1500 to 1:100, on an average does not exceed ±3-5%. For ratios greater than 1:1500, the error increases sharply, reaching ±10-20%. Moreover, on addition of nickel to solution in amounts greater than 1.55 mg, it starts to be precipitated as $[Ni(NH_3)_6]Br_2$.

It is therefore possible to determine copper with satisfactory accuracy in amounts of 0.05% in nickel.

Determination of Copper in the Presence of Elements Which Accompany It

Apart from copper, metallic nickel and its compounds also contains other metals as impurities (zinc, cobalt, and iron). It was essential to establish the effect of these elements on copper determination. Initially, we carried out tests on solutions containing copper, zinc, and cobalt, but not containing nickel. From the results obtained which are given in Tables 2 and 3, it is clear that cobalt can be present in amounts up to 35 γ/ml, and zinc up to 150 γ/ml.

TABLE 2

| Introduced γ/ml		Found	Error
Cu	Co	Cu γ/ml	γ/ml
2,21	1,95	2,20	−0,01
2,21	35,10	2,20	−0,01
2,21	39,00	2 00	−0,21
2,21	54,60	1,20	−1,01
7,36	25,35	7,35	−0,01
7,36	35,10	7,25	−0,11
7,36	39,00	6,50	−1,14
7,36	44,85	6,00	−1,36

TABLE 3

Introduced γ/ml		Found	Error
Cu	Zn	Cu γ/ml	γ/ml
0,92	20,00	0,90	−0,02
0,92	30,40	0,95	+0,03
0,92	100,30	0,96	+0,04
0,92	150,50	1,10	+0,19
0,92	200,70	1,40	+0,48
0,92	401,30	2,00	+1,08
7,36	100,30	7,40	+0,04
7,36	150,50	7,50	+0,14
7,36	200,70	8,10	+0,74

TABLE 4

Introduced γ/ml			Found	Error
Cu	Ni	Co	Cu γ/ml	γ/ml
2,21	643,26	1,95	2,20	−0,01
2,21	643,26	29,26	2,20	−0,01
2,21	643,26	39,00	2,00	−0,21
7,36	643,26	29,26	7,35	−0,01
7,36	643,26	35,10	7,20	−0,16
7,36	643,26	39,00	6,00	−1,36

TABLE 5

Introduced γ/ml			Found	Error
Cu	Ni	Zn	Cu γ/ml	γ/ml
2,21	643,26	50,20	2,20	−0,01
2,21	643,26	150,50	2,25	+0,04
2,21	643,26	200,70	2,50	+0,29
7,36	643,26	50,20	7,35	−0,01
7,36	643,26	150,50	7,60	+0,14
7,36	643,26	200,70	8,90	+1,54

When large amounts of nickel and cobalt were simultaneously present in solution, good results were obtained, similar to those obtained previously (see Tables 1 and 2), as can be seen from Table 4.

As can be seen from Table 4, in the presence of large amounts of cobalt, the optical density of the solution decreases appreciably. This can be explained by the formation of a more stable complex (instability constant $K = 6 \cdot 10^{-36}$) than the corresponding complexes of nickel and copper; this complex does not absorb in the wave-length region $\lambda = 365-380$ mμ.

Similar experiments were carried out on solutions containing large amounts of nickel and zinc simultaneously. Results are given in Table 5.

As can be seen, in this case, zinc can be present in amounts up to 150 γ/ml. Thus, the presence of such impurities as cobalt and zinc as well as copper, has practically no effect on copper determination in nickel. Nickel and its compounds usually contain iron, which strongly distorts results of copper determinations. Attempts to complex all the iron, or to reduce it to the ferrous state, did not give positive results. Reduction proceeds quantitatively, but the ammonia complex of ferrous iron immediately formed, exhibits strong absorption in the region $\lambda = 365-380$ mμ.

After a number of tests it was established that iron can be completely co-precipitated with partially precipitated nickel hydroxide. When this is done, as our experiments showed, copper may also be co-precipitated. To avoid this, we reduced copper beforehand to the cuprous state. In this state, copper stays in solution. In this case, experimental procedure was as follows: in a 50 ml beaker was placed a known amount of solution with a given content of copper and nickel respectively; to this was added 2 ml of 1% ascorbic acid solution, and 2 ml of a saturated potassium bromide solution; this mixture was brought to the boil and hydroxides precipitated with ammonia (1:5). Solution plus precipitate was heated for a further 2-3 minutes and the whole rapidly filtered through a small filter into a 50 ml standard flask. The precipitate on the filter was washed with a small amount of hot distilled water. The reference solution was treated in exactly the same way. To the filtrate was added up to 25 ml of ammonia (1:1), and, after 30 minutes, optical densities were measured. The results obtained are adduced in Table 6.

TABLE 6

Introduced in γ/ml			Found	Error	Introduced in γ/ml			Found	Error
Cu	Ni	Fe	Cu γ/ml	γ/ml	Cu	Ni	Fe	Cu γ/ml	γ/ml
2,00	2844,0	—	1,90	—0,10	2,00	2275,2	20,50	2,00	0,00
2,00	3233,2	—	2,00	0,00	2,00	2275,2	68,30	1,90	—0,10
2,00	3702,0	—	2,10	+0,10	6,78	2275,2	13,66	6,80	+0,02
2,00	5193,0	—	1,90	—0,10	6,78	2275,2	40,98	6,75	—0,03
6,78	5193,0	—	6,70	—0,08	6,78	2275,2	80,88	6,85	+0,07
0,68	3904,6	—	0,70	+0,02	6,78	2275,2	101,10	6,60	—0,18
0,68	5193,0	—	0,60	—0,08					

TABLE 7

Introduced in γ/ml					Found	Error
Cu	Zn	Co	Fe	Ni	Cu γ/ml	γ/ml
0,68	50,17	9,25	27,32	2137,76	0,70	+0,02
2,03	100,34	19,50	50,54	2137,76	1,95	—0,08
2,03	50,17	9,75	27,32	4008,30	2,00	—0,03
2,03	75,93	19,50	50,54	4008,30	2,15	+0,12
6,78	100,34	19,50	50,54	2137,76	6,90	+0,12
6,78	50,17	9,75	27,32	4008,30	6,75	—0,03

TABLE 8

Weight of nickel sample in mg	Cu found in mg	Corresponding to % Cu	% Cu according to spectrographic results
150	0,0200	0,013	
200	0,0325	0,016	0,01—0,03
250	0,0450	0,018	

TABLE 9

Weight of Ni in mg	Cu added in mg	Amount found in mg	Difference in mg	% Cu
200	0,100	0,135	0,035	0,017
200	0,200	0,230	0,030	0,015
250	0,100	0,140	0,040	0,015
250	0,200	0,238	0,038	0,015

It is clear from Table 6 that practically all the iron is co-precipitated with partially precipitated nickel hydroxide. In addition, by using this technique, it is possible to improve the limiting ratios of copper to nickel appreciably; this is particularly important if the nickel contains less than 0.05% of copper. As can be seen from Table 6, for a ratio of Cu : Ni = 1 : 3300, by resorting to co-precipitation, it is possible to determine copper with a very insignificant error (< 3%). Subsequently, experiments were carried out on synthetic solutions containing all the accompanying elements. Results are given in Table 7.

These results show that traces of copper can be determined quite satisfactorily in nickel and its compounds by this technique.

Analysis of Metallic Nickel Samples

In order to check this method for the colorimetric determination of traces of copper in nickel, which we developed by using synthetic solutions, we proceeded to carry out copper determinations in a sample of nickel, in which 0.01-0.03% of Cu had been found by spectrographic analysis; the sample also contained a few hundredths of a percent of zinc, a few thousandths percent of Co, Fe, Al and Si, and ten-thousandths percent of Pb.

Analytical Procedure. An aliquot of nickel was dissolved in dilute nitric acid and the solution obtained transferred to a porcelain basin; a few ml of concentrated sulfuric acid was added and the whole carefully evaporated to dryness. The sulfates obtained were dissolved in a small amount of hot distilled water, and filtered through a small filter into a 50 ml beaker. The filter was washed with hot distilled water, and wash liquor added to filtrate; 2 ml of a 1% solution of ascorbic acid, 2 ml of a saturated potassium bromide solution were then added, and the whole heated to the boil when the hydroxides were precipitated by addition of a small amount of ammonia (1 : 5). After precipitation heating was continued for a further 2-3 minutes and the solution filtered free of precipitate into a 50 ml standard flask. 25 ml of ammonia (1 : 1) was added and the volume made up to 50 ml with distilled water; after 30 minutes, the solution was placed in a photometer cuvette, and optical density measured.

Exactly the same amount of nickel as that contained in the test sample was added to the reference solution; subsequently, 2 ml of 1% ascorbic acid solution and 2 ml of saturated potassium bromide solution were added and the whole heated to the boil when precipitation of hydroxides was effected by adding exactly the same amount of ammonia (1 : 5), as was used in the case of the test sample. After heating, the precipitate was filtered, 25 ml of ammonia (1 : 1) was added, and the total volume made up to 50 ml. The results obtained are given in Table 8.

In order to check the accuracy of the determination, a known amount of copper was added to the test solution, and the copper contained in the metallic nickel determined colorimetrically by difference. Results are given in Table 9.

From the results given in Table 9, it is clear that they are in good agreement. Analysis may be carried out without evaporating the acid solution to dryness. Nevertheless, in this case, the hydroxides cannot be precipitated with ammonia, since part of it will go to neutralize the free acid, and thereby form a mixture of ammonia and ammonium salts which will hinder precipitation of hydroxides from solution. It is best therefore to precipitate with sodium or potassium hydroxide. Analytical procedure after separation of the hydroxides is the same as in the first instance. The results obtained were no worse; the difficulty when this technique is used, is accurate neutralization of acid solution.

SUMMARY

1. A method has been developed for the colorimetric determination of traces of copper in metallic nickel and its compounds in the ultra-violet region of the spectra; it is based on the absorption of rays of $\lambda = 365$-380 mμ by the ammonia complex of univalent copper. The sensitivity of the method amounts to 0.5 γ / ml of copper for a cell thickness of 2.5 cm.

2. Absorption by the ammonia-bromide complex of copper in the visible and ultra-violet over the wavelength range $\lambda = 450$-300 mμ has been studied, and an absorption curve for this complex drawn.

3. It has been shown that determination of traces of copper can be carried out for ratios of accompanying elements of Cu : Ni : Co : Zn = 1 : 1500 : 30 : 75 without preliminary separation; by precipitation of traces of iron with part of the nickel as hydroxide, it is possible to increase ratios of Cu : Ni at which copper can still be determined to 1 : 4,000. A method has been worked out for keeping copper in solution during precipitation of iron and nickel.

4. The method has been checked on a sample of metallic nickel. Analytical procedure is described.

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* T. p. = C. B. Translation pagination.

PART 12. * SIMULTANEOUS DETERMINATION OF CARBON, HYDROGEN, SILICON, AND HALIDES

V. A. Klimova and E. G. Bereznitskaya

Determination of halogens in halogen-containing organosilicon compounds is carried out independently of C, H, and Si, or simultaneously with Si. Methods for halogen determination differ according to whether halogen in the compound is directly connected to silicon or is found in the organic radical [1-4]. In the first instance, the material is usually first hydrolyzed and then the halogen is determined gravimetrically or volumetrically. Nevertheless, such determinations can be troublesome if there are two halogen atoms connected with the silicon, and even more so when there are three halogen atoms involved. The polymerized siloxanes formed in such cases evelops hitherto undecomposed material and prevents quantitative hydrolysis. Dissolving the compound in ether or alcohol beforehand does not always help one to get better results..

In cases where the halogen is not connected to silicon but to carbon, one cannot just resort to simple hydrolysis; more profound decomposition is required here; usually this is carried out by fusing the material in a nickel bomb with sodium peroxide [5, 6]. When this melt has been dissolved, it is possible to determine halogen and silicon simultaneously; this is the advantage of this particular method. In addition, since fusion is carried out in a bomb, it is possible to analyze volatile compounds. All the same, the large amount of reagents (in comparison with the amount of test sample) which has to be used for fusion will introduce errors as a result of the large amount of salts in the solution of melt, and insufficient purity of the reagents used.

With such compounds, if one only wants to determine halogen, good results can be obtained by means of Korshun and Chumachenko's method [7] — by fusing the material in a steel bomb with metallic potassium.

Determination of carbon and hydrogen in halogen-containing organosilicon compounds is carried out by classical methods, but the results obtained are often unsatisfactory. Usually therefore, research workers confine themselves to determining halogen alone.

Thus, at present, there is no method available which is fairly simple and reliable for the determination of the elements in halogen-containing organosilicon compounds. Another difficulty the analyst comes up against when dealing with these compounds is the extreme instability of some of them with respect to water. In such cases, the possibility of carrying out a simultaneous determination of all the elements, or, at least a few of them, on one aliquot assumes particular importance, since such a determination would allow one to confine oneself to a small amount of test material. The present article is devoted to simultaneous determination of the elements — carbon, hydrogen, silicon, and halogen. In a previous article we described a method for simultaneous determination of carbon, hydrogen, and silicon, in compounds not containing halogens [8, 9]. Combustion of the material is carried out by the rapid method in the presence of chromic oxide on asbestos as catalyst. The catalyst is placed directly in the vessel used for decomposition. Carbon and hydrogen are determined as usual, while the silicon is calculated from the weight of silicon dioxide which is formed in the decomposition vessel. This article is a logical development of this method, and also of the method of Korshun and Sheveleva [10], for simultaneous determination of carbon, hydrogen, and halogen by rapid combustion. In this method, halogen is trapped by silver at 550° in a special apparatus outside the combustion tube, and is determined from the increase in weight of the silver. A platinum contact is placed in the combustion tube, for without it, results for carbon determination are low.

Halogen-containing organosilicon compounds, as our experiments showed, exhibit their own characteristic thermal decomposition under the conditions of rapid combustion;accordingly, simple combination of the methods described above is out of the question.

* For Part 11, see J. Anal. Chem. 6, 358 (1955) (C. B. translation p. 347).

Thermal decomposition of halogen-containing organosilicon compounds in the absence of oxidizing agents, and of sufficient oxygen — the state of affairs which holds when combustion is carried out by the rapid method — differs from one class of compounds to the other. Thus, compounds containing C, H, Si, and Cl, and in which the halogen is connected to carbon, and not to silicon, burn without formation of silicon carbide, and results for all four elements are satisfactory, even without addition of oxidizing agent. The halogen which is split off during thermal decomposition, apparently, itself plays the part of an oxidizing agent, and prevents carbide formation.

Decomposition takes a different path when the organosilicon compound contains halogen connected to silicon. In these cases during decomposition, silicon tetrahalide is formed; in addition, in some cases, carbide formation also occurs. The silicon tetrahalide may be carried out of the combustion vessel and absorbed by the silver; as a result determination of both silicon and halide becomes impossible (Table 1). Nevertheless, if the molecule contains enough hydrogen — as our experiments showed, not less than 3% — then the water which is formed during combustion decomposes the silicon tetrahalide to give SiO_2 and the corresponding hydrogen halide, and its formation will not interfere with the determination. Materials which contain less hydrogen than that indicated above can often be analyzed by adding a small amount of water (3-5 mg) to the test aliquot (Table 2). In such cases however decomposition of the compound by water may precede thermal decomposition of the molecule. As a result of interaction with water, the chlorosilane will change over into polymerized siloxanes, and the thermal decomposition of the latter, as Rochow has already pointed out, is usually accompanied by formation of silicon carbide; consequently, combustion of these compounds can only be carried out in the presence of oxidizing agents or catalysts. Accordingly we had to clarify the possibility of carrying out the analysis in the presence of a catalyst which we had adopted, viz. chromic oxide on asbestos *.

Chromic oxide is known to react with chlorine at high temperatures [11]. It may be postulated therefore, that the catalyst which we have used before — chromic oxide on asbestos — may react with the halogen of an organic compound during the thermal decomposition of the latter. Actually, when combustion of hexachloroethane is carried out in the presence of the catalyst Cr_2O_3 on asbestos, we observed the formation of dark brown drops which settle out on the cold parts of the combustion tube. The weight of beaker plus catalyst decreased by 100-500 μg, while no such brown vapors were formed when halogen-containing organic compounds which also contain hydrogen were decomposed under these same conditions, or when samples of hydrogen chloride were evaporated; in these cases the weight of the beaker changed inappreciably. This can apparently be explained by the hydrolyzing effect of water on the halogen compounds of chromium formed (Table 3).

The results obtained show that analysis of halogen-containing organosilicon compounds should be carried out differently, according to the structure of the test compound, and also permit one to develop a method for simultaneous determination of carbon, hydrogen, silicon, and halogen in the various classes of these compounds.

Analysis of Organosilicon Compounds in Which Halogen is Linked to Carbon

Test sample is weighed out into a quartz beaker 70-80 mm long and 4-5 mm diameter, or into a glass ampoule, if the material is volatile. 100-200 mg of asbestos calcined at 1200° is introduced into this beaker and the whole re-weighed. When an ampoule is used, it is placed in a beaker with asbestos, with its open end on the bottom of the beaker, so that all the ampoule is inside the beaker. If the ampoule was weighed sealed, then the tip can be broken on the bottom of the beaker.

Beaker plus sample are placed in the combustion tube which contains a contact made from platinum foil. Three absorbent trains are then connected up: the first to be connected up is made of high melting glass or quartz; it is filled with metallic silver and is heated in a special oven to 500-550°; the next in order, is a train for water adsorption; finally the apparatus for absorbing carbon dioxide. In this case, when nitrogen is present in the test material, an absorbent vessel for nitrogen oxides is connected between the last two absorbent vessels. Combustion is then commenced. When combustion is complete the three absorbent vessels and beaker used for combustion are weighed. Silicon is calculated from the increase in weight of the beaker as a result of formation of silicon dioxide; halogen from the increase in weight of the silver; and carbon and hydrogen, as usual (Table 4).

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* Since polymerized siloxanes are not volatile, a thin layer of chromic oxide on asbestos is sufficient for their complete oxidation.

TABLE 1

Material	% Halogen Found	% Halogen Calculated	% Silicon Found	% Silicon Calculated	% C Found	% C Calculated	% H Found	% H Calculated
Bis-(trichlorosilyl) dichloromethane Cl_3—SiC—$SiCl_3$ ‖ Cl_2	108,80 104,50	80,63	0,57 None	15,96	3,59 3,41	3,41	None 0,13	None
Bis-(trichlorosilyl)- chloromethane $Cl_3SiCHClSiCl_3$	81,92 102,17	78,20	Traces None	17,71	3,78 3,87	3,77	0,78 0,28	0,32

TABLE 2

Material	% Halogen Found	% Halogen Calculated	% Silicon Found	% Silicon Calculated	% C Found	% C Calculated	% H Found	% H Calculated
Bis-(trichlorosilyl) dichloromethane	80,39 80,28	80,65	16,05 16,37	15,96	3,35 3,47	3,41	None None	None
Bis-(trichlorosilyl) chloromethane	78,06 78,53	78,20	17,67 17,76	17,68	3,77 3,56	3,79	0,39 0,28	0,32

TABLE 3

Material	Sample weight in mg	Change in weight of beaker in mg	% Halogen Found	% Halogen Calculated	% H Found	% H Calculated	% C Found	% C Calculated
Naphthalene	8,92 10,01	−20 −30	—	—	6,26 6,33	6,29	93,80 93,84	93,71
Hexachloroethane	10,53 8,27 10,26 8,23	−560 −200 −110 −90	83,95 86,94 91,62 90,42	89,87	—	—	10,13 10,23 10,08 10,12	10,12
$C_{13}H_{17}ClO$	10,52 10,68	−60 −30	12,36 12,76	13,00	6,23 6,34	6,23	57,23 57,32	57,27
Hydrochloric acid	17,65 18,73 20,13 19,24	−10 −0 −10 +20	—	—	—	—	—	—

Analysis of Compounds in Which Halogen is Connected to Silicon

The majority of compounds of this type can be analyzed by the method described above (Table 5). Materials which contain less than 3% hydrogen are exceptions to this. When compounds of this type are analyzed a drop or two of water (3-5 mg) is added to the beaker containing the test material plus asbestos, and the whole re-weighed. During final calculations, the weight of water added is subtracted from the weight found. For the rest, the analytical procedure is the same as usual (Table 6).

TABLE 4

Material	Found C%	Calculated C%	Difference ΔC%	Found H%	Calculated H%	Difference ΔH%	Found Si%	Calculated Si%	Difference ΔSi%	% Halogen Found	% Halogen Calculated	Difference in Halogen
Dimethylchloromethylethylsilane	44,04 / 44,52	43,93	+0,11 / +0,59	10,04 / 9,78	9,58	+0,46 / +0,20	20,24 / 20,16	20,55	−0,34 / −0,39	25,98 / 26,13	25,94	+0,04 / +0,19
Trimethyl-γ-chloropropylsilane	47,81 / 47,96	47,81	−0,05 / +0,15	9,88 / 10,02	10,03	−0,05 / −0,01	18,83 / 18,51	18,63	+0,20 / −0,12	23,50 / 23,40	23,52	−0,02 / −0,12
Methyliodomethyldipropylsilane	35,80 / 35,72	35,56	+0,24 / +0,16	7,01 / 7,08	7,09	−0,08 / −0,01	10,47 / 10,41	10,39	+0,02 / +0,02	47,31 / 46,63	46,96	+0,35 / −0,33
1,2-Bis-trimethylsilyl-1,2-dibromoethane	28,94 / 28,96	28,91	+0,03 / +0,05	6,14 / 6,08	6,07	+0,07 / +0,01	16,38 / 16,28	16,91	−0,53 / −0,63	48,18 / 48,15	48,11	+0,07 / +0,04

TABLE 5

Material	Found C%	Calculated C%	ΔC%	Found H%	Calculated H%	ΔH%	Found Si%	Calculated Si%	ΔSi%	Found Cl%	Calculated Cl%	ΔCl%
Dimethylbutylchlorosilane	47,88 / 47,77	47,81	+0,07 / −0,04	10,00 / 10,00	10,03	−0,03 / −0,03	18,94 / 18,84	18,64	+0,30 / +0,20	23,27 / 23,03	23,52	−0,25 / −0,49
Methylnaphthyldichlorosilane	54,51 / 54,96	54,77	−0,26 / +0,19	4,27 / 4,22	4,18	+0,09 / +0,04	11,92 / 11,78	11,65	+0,27 / +0,13	29,10 / 29,70	29,40	−0,30 / +0,30
Propyldichlorosilane	25,32 / 25,08	25,18	+0,14 / −0,10	5,54 / 5,68	5,63	−0,09 / +0,05	20,07 / 19,64	19,63	+0,44 / +0,01	49,11 / 49,81	49,56	−0,45 / +0,05
n-Butyl(β-chloroethyl)dichlorosilane	32,98 / 33,08	32,81	+0,17 / +0,27	6,02 / 6,03	5,97	+0,05 / +0,06	12,33 / 12,91	12,79	−0,46 / +0,12	48,43 / 49,07	48,43	+0,07 / +0,24
Phenyl-α-cyanoisopropoxydichlorosilane	46,41 / 46,49	46,16	+0,14 / +0,18	4,46 / 4,49	4,26	+0,20 / +0,23	10,87 / 10,75	10,80	+0,07 / −0,05	27,08 / 27,00	27,25	−0,17 / −0,25

TABLE 6

Material	Found C%	Calculated C%	ΔC%	Found H%	Calculated H%	ΔH%	Found Si%	Calculated Si%	ΔSi%	Found Cl%	Calculated Cl%	ΔCl%
Bis-(trichlorosilyl)dichloromethane	3,68 / 3,47	3,41	+0,27 / +0,06	Нет / b	Нет		16,05 / 16,37	15,97	+0,08 / +0,40	80,39 / 80,26	80,01	−0,22 / −0,35
Bis-(trichlorosilyl)chloromethane	3,77 / 3,36	3,78	−0,01 / −0,22	0,39 / 0,28	0,32	+0,07 / −0,04	17,67 / 17,76	17,70	−0,03 / +0,06	78,05 / 78,53	78,20	−0,15 / +0,33
1,2-Bis-(trichlorosilyl)chloroethane	7,11 / 7,20	7,25	−0,08 / −0,04	1,04 / 0,96	0,91	+0,10 / +0,05	16,87 / 16,92	16,95	−0,08 / −0,03	75,30 / 75,64	74,89	+0,41 / +0,75
β-chloroethoxytrichlorosilane	11,37 / 11,41	11,23	+0,14 / +0,18	1,98 / 2,02	1,89	+0,09 / +0,13	13,14 / 13,10	13,11	+0,03 / −0,01	65,57 / 65,82	66,29	−0,72 / −0,67

TABLE 7

Material	Found C%	Calculated C%	ΔC%	Found H%	Calculated H%	ΔH%	Found Si%	Calculated Si%	ΔSi%	Found Cl%	Calculated Cl%	ΔCl%
1-Trichlorosilyl-1-dichlorosilylethane	9,34 / 9,31	9,15	+0,19 / +0,16	1,69 / 1,67	1,92	−0,23 / −0,25	21,34 / 21,19	21,40	−0,07 / −0,21	67,94 / 68,21	67,53	+0,41 / +0,68
1,4-bis-(trichlorosilyl)butane	15,10 / 14,91	14,78	+0,32 / +0,13	2,38 / 2,29	2,48	−0,10 / −0,19	17,46 / 16,79	17,29	+0,17 / −0,50	65,82 / 65,12	65,45	+0,37 / −0,33
α-Methylisobutylchlorosilane	23,13 / 22,93	23,14	−0,01 / −0,15	4,43 / 4,58	4,37	+0,06 / +0,21	13,50 / 13,50	13,52	−0,02 / −0,02	50,65 / 51,02	51,24	−0,39 / −0,22
Diethylisobutylchlorosilane	47,55 / 47,52	47,81	−0,26 / −0,29	10,04 / 9,95	10,03	+0,01 / −0,08	18,39 / 18,09	18,64	−0,25 / −0,55	23,50 / 23,32	23,52	−0,02 / −0,20
Chlorobutyltrichlorosilane	21,14 / 21,44	21,44	−0,30 / 0,00	2,36 / 2,58	2,71	−0,35 / −0,13	12,56 / 12,43	12,54	+0,02 / −0,11	62,97 / 63,45	63,34	−0,34 / +0,04
Propyldichlorosilane	25,32 / 25,08	25,18	+0,14 / −0,10	5,54 / 5,68	5,63	−0,09 / +0,05	20,07 / 19,64	19,63	+0,18 / −0,34	49,11 / 49,61	49,56	+0,45 / +0,05

Formation of silicon carbide was observed during attempts to analyze some compounds by the usual method. Silicon carbide was most often formed during analysis of compounds containing three atoms of halogen on one silicon atom, and during analysis of materials which have both hydrogen and halogen on the silicon atom. Such compounds are the most difficult from an analytical point of view, since their combustion cannot be carried out in the absence of chromic oxide. Nevertheless, as already pointed out, in the presence of water, chromic oxide does not interact or hardly interacts at all with halogen, while the small amount of the halogen compound of chromium formed is completely broken down by the water under the experimental conditions. When such compounds are to be analyzed therefore, the following procedure should be adopted.

To the aliquot of test material is added a small amount of chromic oxide on asbestos, a layer of asbestos is then laid down and the whole weighed. A drop of water is placed on the asbestos and the whole re-weighed. Combustion is then carried out as usual. When calculations are made of the water content on the basis of the increase in weight of the apparatus used for absorbing water, the weight of water added at the beginning is subtracted. By means of this method we succeeded in determining the four elements in compounds for which we could not get satisfactory results by means of other methods (Table 7)*.

SUMMARY

1. Decomposition of halogen-containing organosilicon compounds under the conditions used for rapid combustion has been studied.

2. A method has been worked out for the simultaneous determination of carbon, hydrogen, silicon, and halogen in various organosilicon compounds. The accuracy of the method for carbon and hydrogen is ±0.3%, for silicon ± 0.4%, and for halogen ± 0.5-0.6%.

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* Most of the compounds which are listed in the article were kindly given to us by Corresponding Member
A. D. Petrov and his coworkers.
** T. p. = C. B. Translation pagination.

ISOLATION AND SEPARATION OF A MIXTURE OF FORMALDEHYDE AND ACETALDEHYDE BY MEANS OF DIMEDONE

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Isolation and identification of individual compounds from complex organic mixtures is extremely important in studies on the mechanism of chemical reactions. This is of special importance when labeled atoms are used for studying the mechanism. In such cases the reliability of isotopic analysis depends on the chemical purity of the product isolated and on the conditions used for isolating it; under these conditions the possibility of isotopic dilution of the product should be excluded.

During studies of the reaction mechanism of the oxidation of carbohydrates, considerable attention is given to the study of the part played by aldehydes, the mechanism of their formation, their behavior, etc. Accordingly, research workers used various techniques and methods for quantitative determination and identification of aldehydes.

The most convenient method for identifying aldehydes is to make use of the specific group of the reagent dimedone (5,5-dimethylcyclohexane-dione-1,3 [1]).

On reacting with aldehydes, dimedone forms enol compounds:
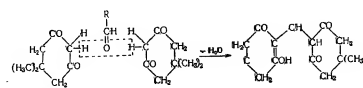
On heating the enol derivatives with dilute mineral acids, acetic acid, acetic anhydride, or absolute alcohol, ring closure occurs with separation of water and formation of so called "anhydrides":
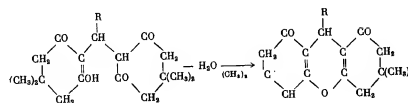
Formaldehyde is an exception to this rule; it only forms the enol compounds; the "anhydride" can only be prepared by prolonged heating of the enol with concentrated acids.

Both groups of aldehyde-dimedone derivatives are crystalline compounds with characteristic melting points.

In working with aldehydes, labeled with radio-carbon, the dimedone derivatives are very convenient products, since they are relatively easily isolated from complex organic mixtures, and it is fairly easy to prepare good samples from them for measurement of radioactivity. In addition, it is possible to separate the pure formaldehyde derivative from a mixture of the derivatives of different aldehydes. We have already pointed out that formaldehyde, in contrast to other aldehydes, only forms the enol, which is readily soluble in weak alkali solutions. This property is used for separating the formaldehyde product from the derivatives of the higher aldehydes.

As a consequence of the slight solubility of dimedone in water, precipitation of mixtures of formaldehyde and acetaldehyde is carried out from aqueous-alcohol solutions in the presence of mineral acid. The products isolated are washed with water and dilute alcohol to remove sulfuric acid and dimedone, and then treated with an alkali solution. The enol product of formaldehyde dissolves in the alkali, while the "anhydride" of acetaldehyde remains in the precipitate. The formaldehyde derivative is removed and the solution acidified until weakly acid. This method of separation permits one to get very pure products in a fairly good yield.

In order to separate formaldehyde and acetaldehyde formed during oxidation of hydrocarbons, we carried out a series of tests to check on the completness of the separation of the derivatives of formaldehyde from acetaldehyde, using acetaldehyde labeled with radio-carbon.

The mixture of formaldehyde and labeled acetaldehyde was treated in a 50% alcoholic solution with dimedone in the presence of sulfuric acid. After isolation of the derivatives of formaldehyde and acetaldehyde, they were washed and recrystallized from 50% alcohol. Melting points as well as the specific activity (α impulses/min-mg) of the compounds were then determined. Results of these experiments are given in Table 1.

TABLE 1

Checking on Completness of Separation of CH_2O from CH_3CHO

Compound	After isolation	I Recrystallization		II Recrystallization		III Recrystallization	
		Melting Point in °C	α	Melting Point in °C	α	Melting Point in °C	α
CH_3CHO	1. 171—173°	173	100	173.5	102	173.5—174	102
	2. 171—173°	173	200	173	205	173.5—174	205
CH_2O	1. 186—187°	187.5—8	0	188.5	0	188.5—189.5	0
	2. 186—187°	187.5—8	0	188	0	189	0

As the results in Table 1 show, formaldehyde is completely inactive when the specific activity of the acetaldehyde is comparatively high. This indicates that formaldehyde has been isolated in a very pure state from acetaldehyde.

Similar results were obtained in the case of a mixture of two labeled dimedone derivatives. Results of these tests are given in Table 2.

Accordingly, this method ensures complete separation of mixtures of dimedone products, and it would appear that it can be used for the separation of labeled aldehydes; nevertheless, tests showed that this method is not really applicable for the separation of the derivatives of labeled aldehydes.

We precipitated the same preparation of labeled acetaldehyde from an aqueous-alcohol solution with dimedone in the presence of H_2SO_4 as described above, and also from an aqueous solution with 2,4-dinitro-phenylhydrazine in the presence of HCL. After isolation of the dimedonate and the hydrazone, their specific

activities were determined. In addition another aliquot of the same acetaldehyde $C^{14}H_3CHO$, was subjected to combustion to give CO_2 and the specific activity of the $BaCO_3$ formed measured. Results are given in Table 3.

TABLE 2

Separation of the Mixture of Labeled Dimedonates of CH_2O and CH_3CHO

Compound	Specific activity in impulses minutes$^{-1} \cdot mg^{-1}$			
	Original products	After separation		
		I Recrystallization	II Recrystallization	III Recrystallization
CH_3CHO	195	194	195	195
CH_2O	72	71	72	72

TABLE 3

Determination of the Specific Activity of CH_3CHO by Various Methods

Compound measured	Specific activity in impulses minutes$^{-1} \cdot g^{-1}$	
	Compound	On one atom of standard compounds
1. Dimedonate isolated from alcoholic solution	120	175
2. Hydrazone	167	191
3. $BaCO_3$	97	194
4. Dimedonate isolated from aqueous solution	132	192

The last column in Table 3 contains the values of the specific activity referred to a standard compound ($BaCO_3$), and related to one labeled atom of acetaldehyde. This calculation was based on the formula

$$\alpha_{atom} = \alpha_{compound} \frac{M_{compound}}{197.4}$$

where $M_{compound}$ is the molecular weight of the compound being measured (the dimedone derivative or hydrazone), while 197.4 is the molecular weight of $BaCO_3$.

It is clear from this table that the specific activity of acetaldehyde calculated on the basis of the standard compound in the case of measurements on the dimedone derivative isolated from alcoholic solution, differs considerably from the specific activity found by measurements carried out on hydrazone and $BaCO_3$.

Replicate experiments showed that the specific activity of the dimedonate is 10-20% lower than the values which the hydrazone and carbonate give.

It was found that the drop in specific activity of the dimedonate when derivatives are made in alcohol or alcoholic mixtures may be the result of the fact that the alcohol itself contains aldehyde. In fact, polarographic analysis of the alcohol showed that acetaldehyde was present, its concentration varying in a fairly wide range (up to 4-6 mM/liter).

The alcohol was freed from aldehydes by treating it with 2,4-dinitrophenylhydrazine. When alcohol so treated was used, the specific activity of the dimedone derivative increased somewhat; nevertheless, its activity still remained lower than that of the hydrazone and $BaCO_3$.

This is probably connected with oxidation of C_2H_5OH to CH_3CHO on heating with H_2SO_4 in the air; possibly isotopic exchange occurs between alcohol and aldehyde, or it may be for some other reasons. Obviously, the dimedonate method can only be used if factors which lead to isotopic dilution of acetaldehyde are excluded.

Naturally, we ceased to prepare dimedonates in alcoholic solutions. We therefore prepared them in aqueous solution. Dimedone is only sparingly soluble in cold water (10-15 mg in 100 ml at 20°); nevertheless, in the presence of acids and on heating, its solubility increases. At 100°, upwards of 5 g dissolves in 100 ml water.

Using the enhanced solubility of dimedone in water on heating, we treated the aldehydes (or their mixtures) first, with an aqueous solution of dimedone saturated with the latter at 20°, then crystalline dimedone (2 g for 50 ml) was added, followed by concentrated H_2SO_4 (5 ml for 50 ml of solution); the whole was then heated to the boil in a flask fitted with a reflux condenser and boiling continued for 3-4 hours. Under these conditions, the derivatives of the aldehydes crystallize out immediately in the form of solid compounds which float on top of the liquid. In view of the fact that unreacted dimedone is precipitated on cooling the mixes with the dimedonates, we isolated the precipitate directly from hot solution. When filtration is carried out on a filter funnel specially adapted for filtering hot, or on a porous filter with suction, it is possible to crystallize out only an insignificant amount of dimedone. Dimedone readily dissolves in slightly warm alkali solutions. This enabled us to separate the acetaldehyde derivative from the derivative of formaldehyde and dimedone. Separation of the formaldehyde derivative from dimedone was carried out after isolating the solid precipitate by washing the latter with 50% alcohol solution. Determination of the specific activity of the acetaldehyde dimedonate separated by such a technique, showed good agreement with results obtained by other methods (see Table 3).

A check on the cleanness of separation of CH_2O and CH_3CHO gave similar results to those described above. Special experiments with marked formaldehyde dimedonate showed complete separation of dimedone from its derivative on treating it with 50% alcohol and recrystallization.

The method described can be applied for isolating and separating mixtures of formaldehyde and acetaldehyde. The pure formaldehyde derivative can be isolated in yields of up to 90%, while that of acetaldehyde can be isolated in yields up to 70%. Obviously, the formaldehyde derivative partially dissolves in alcoholic solution during the process of freeing it from dimedone, while acetaldehyde volatilizes to a considerable extent from the aqueous solution during boiling of the reaction mixture in the preparation of the dimedonates.

It should be pointed out that this method could be successfully used for isolation and separation of derivatives of formaldehyde and acetaldehyde even in cases where their mixture contains up to 20% of other higher aldehydes. Special experiments showed that from a mixture containing 20% of the dimedone derivative of propionaldehyde, the dimedonate of acetaldehyde could be isolated perfectly pure by 3-4 crystallizations from 50% alcohol.

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APPLICATION OF β-HYDROXYNAPHTHOIC ALDEHYDE
IN ANALYTICAL CHEMISTRY

PART 2. A NEW SEMI-MICRO GRAVIMETRIC METHOD FOR THE DETERMINATION OF COPPER

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In a previous communication [1], we demonstrated the possibility of determining magnesium quantitatively by means of β-hydroxynaphthoic aldehyde.

Under certain conditions, in ammoniacal, or, in certain cases, in alkaline solutions, this reagent gives sparingly soluble complex compounds with many (except cadmium) divalent metals such as: Cu^{2+}, Be^{2+}, Mg^{2+}, Ca^{2+}, Zn^{2+}, Sr^{2+}, Ba^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Pd^{2+}. The characteristic crystals formed are suitable for the qualitative determination of divalent cations (work along these lines continues).

In the work described in the present article we aimed at studying the conditions of formation of the inner complex copper compound of β-hydroxynaphthoic aldehyde, to study its physico-chemical properties, and to establish the optimum conditions for carrying out quantitative determination of copper in various objects by means of it.

EXPERIMENTAL

Preparation of the Copper Complex of β-Hydroxynaphthoic Aldehyde

To 100 ml of a $CuCl_2$ solution (containing 0.1 M salt) was added 50 ml of ethyl alcohol and 10 ml of 25% ammonia solution. The mixture was heated to the boil, after which 200 ml of a molar alcoholic solution of β-hydroxynaphthoic aldehyde was added. Immediately, or after a short time interval, a greenish-grey crystalline precipitate of the copper complex of β-hydroxynaphthoic aldehyde was formed. This material was crystallized three times from acetoacetic ester. Analysis of the compound formed gave the following results.

Found % Cu 15.60; 15.90; C 64.52; 64.85; H 3.45; 3.55.

On the basis of the assumed formula $C_{22}H_{14}O_4Cu$, the following figures were obtained(%): Cu 15.66; C 65.09; H 3.48.

Analysis of the compound for nitrogen gave negative results. The same compound was prepared by the interaction of cupric chloride, pyridine, and β-hydroxynaphthoic aldehyde. Found 64.75% C; 3.54% H.

Formation of the copper complex of β-hydroxynaphthoic aldehyde can be represented by the following scheme:

$$[Cu(NH_3)_4]Cl_2 + 2C_{10}H_6\!\!\begin{smallmatrix}C=H\\O\end{smallmatrix}\!\!-OH + 2H_2O \rightarrow$$

$$\rightarrow C_{10}H_6 \cdots Cu \cdots C_{10}H_6 + 2NH_4Cl + 2NH_4OH$$
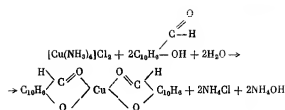
Some of the properties of this copper compound are given in Table 1.

TABLE 1

Properties of the Copper Complex of β-Hydroxynaphthoic Aldehyde	
Color	Grey-green
Solubility in water (15°)	0.002%
Solubility in alcohol (15°)	0.004%
Solubility in ether (15°)	0.022%
Heating in a capillary in air	At 170°, the compound becomes red brown in color, at 248° it decomposes and is converted into a dark brown mass
Behavior to dilute acids	Does not change in 2 N H_2SO_4
Behavior to dilute alkalis	Does not change in 2 N NaOH
Crystal form under the microscope, see diagram below	

Crystals of the complex compound of copper with β-hydroxynaphthoic aldehyde (× 120).

Quantitative Determination of Copper with β-Hydroxynaphthoic Aldehyde

Gravimetric determination of copper by means of β-hydroxynaphthoic aldehyde was first tried out on pure salts. A standard copper solution was prepared by dissolving 1 g of electrolytic copper in a small amount of nitric acid, the solution was carefully diluted and then made up to 1000 ml with water; the final solution then contained 1 mg Cu/ml. To a copper-ammonia solution heated to the boil was added a 2% alcoholic solution of β-hydroxynaphthoic aldehyde, using 1.5-2 ml of the reagent solution per ml of copper solution. The test solution should contain 50% alcohol. A greenish-grey precipitate separated out, filtered after 25-30 min. through a No. 2 or No. 3 glass crucible, washed 3 times with water and dried to constant weight at 115-120°. The conversion factor to Cu^{2+} is 0.1566. Results are given in Table 2.

It is clear from this table that determination of copper by the method described gives fully satisfactory results. The gravimetric method was further checked on alloys containing other metals apart from copper.

Analysis of Brass (59.0% Cu, 39.5% Zn, 1.5% Pb)

0.1 g of alloys was dissolved in concentrated nitric acid by gradual addition of the latter; to the solution obtained was added ammonia; when an insoluble residue was obtained, this was filtered off, carefully washed with water and the filtrate made up to a 100 ml in a standard flask. To 5 ml of the solution thus obtained was added ~3 ml of 95% ethyl alcohol and 1 ml of 25% ammonia; the mixture was heated to the boil, and ~6 ml of a heated 2% alcoholic solution of β-hydroxynaphthoic aldehyde was added. After 2-3 minutes a crystalline

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TABLE 2

Cu taken in mg	Weight of precipitate in g	Cu found in mg	Absolute error in mg
2	0,0126	1,97	—0,03
2	0,0128	2	—
2,5	0,0160	2,5	—
3	0,0182	2,85	—0,15
3,5	0,0216	3,38	—0,12
4	0,0252	3,95	—0,05
4	0,0252	3,95	—0,05

TABLE 3

Volume of test solution in ml	Weight of precipitate in g	Cu found		By electrolysis in %
		In mg	In %	
5	0,0188	2,94	58,8	59
5	0,0188	2,94	58,8	—
10	0,0372	5,83	58,3	—

precipitate settled out. After 25-30 minutes this precipitate was transferred to a No 2 glass crucible, washed 3 times with water and dried at 115-120°. When 10 ml of test solution was taken, the volumes of the reagents indicated were correspondingly increased. Results for determination of copper in brass are given in Table 3.

Thus, this method can give satisfactory results for the determination of copper in alloys by means of β-hydroxynaphthoic aldehyde. Copper was also determined in bronzes of various makes. Al^{3+}, Fe^{3+}, and Cr^{3+} ions were masked with tartaric acid.

0.1 g of test alloy containing copper was dissolved in nitric acid; the solution obtained was made up to 100 ml with water in a standard flask. To 10 ml of this solution was added 0.5 ml of 10% tartaric acid solution, 5 ml of alcohol, and 3 ml of 25% ammonia. The liquid was heated to the boil and then ~15 ml of 2% alcoholic solution of β-hydroxynaphthoic aldehyde added. The mixture was then re-heated until precipitate formed. After 25-30 minutes the precipitate was transferred to a No. 2 or No. 3 glass crucible, carefully washed 3-4 times with water, and dried at 115-120°. On standing, the solution gradually darkened and acquired a brownish color, this however did not seem to be reflected in the analytical results.

On determining copper in bronze containing 86.86% Cu, 8.71% Al, 2.62% Fe, 1.56% Mn, 0.14% Zn, we found 86.76, 87.97 and 86.44% Cu.

By introducing tartaric acid into solution, ions such as Fe^{3+}, Mn^{2+}, Al^{3+}, and Zn^{2+} did not interfere with copper determination. The method is distinguished by its simplicity and the rapidity with which it can be carried out. Determination of copper in the presence of nickel is impossible as the result of co-precipitation of the latter with β-hydroxynaphthoic aldehyde. It is necessary to remove nickel beforehand with dimethylglyoxime.

Determination of Copper in Malachite and Copper Sands

0.1-0.2 g of malachite was dissolved on heating in 0.5-1 ml of nitric acid (sp. gr. 1.40); water (10-15 ml) was then added. When an insoluble residue was obtained then the latter was filtered off, washed with hot water and the filtrate made up in a standard flask to 100 ml with water. In all cases 10 ml of test solution was taken; to this was added from 1 to 3 ml of 10% tartaric acid solution; the analysis was then carried out as described for bronze analysis. Results are given in Table 4.

For determination of copper in copper sands, aliquots of 0.5-2 g of test material, depending on the copper content, were boiled with 8 ml of HNO_3 (sp. gr. 1.40) for 10 minutes; the liquid was filtered off from insoluble material into a 100 ml standard flask; filter plus residue was carefully washed with hot water; the filtrate was made up to 100 ml with water. The procedure then followed was the same as that described for analysis of alloys. Results are given in Table 5.

TABLE 4

Number of malachite sample	Weight of aliquot	$C_{22}H_{14}O_4Cu$ in g	Cu found in %	Cu found by electrolysis in %
1	0.1000	0.0344	53.87	53.75
	0.1000	0.0346	54.18	53.75
2	0.2000	0.0298	23.33	23.45
	0.2000	0.0302	23.65	23.45

TABLE 5

Number of sand sample	Weight of aliquot	Weight of precipitate $C_{22}H_{14}O_2Cu$ in g	Found Cu in %	Found Cu by electrolysis in %
1	2.0000	0.0226	1.77	1.78
	2.0000	0.0232	1.82	1.78
2	0.5000	0.0188	5.89	5.51
	0.5000	0.0186	5.82	5.51
3	2.0000	0.0270	2.11	1.73
	2.0000	0.0264	2.06	1.73
4	1.0000	0.0230	3.60	3.42
	1.0000	0.0230	3.60	3.42

SUMMARY

1. An inner complex salt formed between copper and β-hydroxynaphthoic aldehyde has been prepared and some of its properties studied.

2. A new semi-micro gravimetric method has been developed for the determination of copper in alloys and minerals, in which copper is weighed as $C_{22}H_{14}O_4Cu$ (conversion factor to $Cu^{2+} = 0.1566$).

3. Analysis is fairly accurate and rapid. Elements accompanying copper, such as, Fe, Mn, Al, and others can be kept in solution by means of tartaric acid.

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* T. p. = C. B. Translation pagination.

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CHROMOTROPIC AZO DYES AS REAGENTS FOR TRIVALENT THALLIUM

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Comparatively few reagents are known at present for trivalent thallium. Among organic reagents one should mention methyl violet [1], dithizone [2], and benzidene [3].

We investigated the possibility of using certain chromotropic azo dyes as reagents for trivalent thallium:
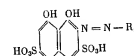
where R may be the following radicals:
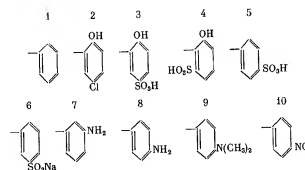
We used 0.1% aqueous solutions of these reagents; Reagent 8 was used in alcoholic solution. Reactions were carried out as follows: to 1 ml of a solution of a salt of trivalent thallium were added 0.1 ml of 2 N acetic acid and 1-2 drops of reagent solution. After shaking, the test tube plus solution was heated on a water bath for a few minutes at 35-40°. When the reaction was carried out in this way, all the chromotropic dyes gave color changes in the presence of trivalent thallium (Table 1).

Thus, all the reagents tested give color reactions with salts of trivalent thallium under the conditions indicated. The reactions will also occur in the cold, but slowly. Only Reagent 9 gives a positive reaction in hydrochloric acid media as well. Salts of univalent thallium do not give a positive reaction. Next we determined the limiting ratios at which thallium can be detected in the presence of other cations with Reagents 3, 6 and 9 (Table 2).

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These results show that it is possible to detect thallium directly in the presence of other cations. In most cases, best limiting ratios were observed when Reagent 9 was used. Accordingly in subsequent experiments we concentrated entirely on the use of this reagent. We used this reaction for colorimetric determination of trivalent thallium salts. In a series of identical test tubes were placed 1 ml of standard solution, containing

TABLE 1

Reactions for Trivalent Thallium with Chromotropic Azo Dyes

Reagent number	Color		Limit of identification of Tl^{3+} in γ/ml	Limiting concentration
	Control	Tl^{3+}		
1	Rose	Yellow	2	1:500000
2	Rose	Yellow	1	1:1000000
3	Violet	Rose	5	1:200000
4	Rose	Yellow	3	1:330000
5	Rose	Yellow	1	1:1000000
6	Rose	Yellow	1	1:40000
7	Rose	Yellow	25	1:100000
8	Rose	Yellow	10	1:20000000
9	Blue	Violet	0.05	1:50000
10	Rose	Yellow	20	

TABLE 2

Limiting Ratios in Detection of Thallium

Cation	Reagent			Cation	Reagent		
	3	6	9		3	6	9
	Limiting ratio of Tl^{3+} to cation				Limiting ratio of Tl^{3+} to cation		
Zr^{IV}	1:30	1:100	1:60	Mg^{2+}	1:900	1:100	1:10000
La^{3+}	1:100	Does not interfere	1:1000	Ca^{2+}	1:400	1:100	1:4000
Ce^{3+}	1:400		1:5000	Mn^{2+}	1:500	1:150	1:5000
Al^{3+}	1:200	1:850	1:200	Co^{2+}	1:10	1:10	1:50
Cr^{3+}	1:20	1:1	1:900	Ni^{2+}	1:20	1:100	1:5000
Fe^{3+}	1:10	1:20	1:5000	Cu^{2+}	1:200	1:100	1:5500
Bi^{3+}	1:900	1:800	1:6000	Zn^{2+}	1:20	1:20	1:100
UO_2^{2+}	1:100	1:100	1:300	Hg^{2+}	1:1300	Does not interfere	1:5000
Be^{2+}	1:40	Does not interfere	1:600	Pb^{2+}	1:1200		1:4500

from 1 to 10 γ Tl^{3+}, and to each was added 0.1 ml of 2 N acetic acid, 4 drops of glycerol, and 3 drops of a 0.1% solution of Reagent 9. 1 ml of test solution was treated in exactly the same way, and the color obtained in this case compared with the colors of the series of standard solutions. Results of a large number of determinations showed that it is possible to get fully satisfactory results for the quantitative determination of 1-10γ of Tl^{3+} in 1 ml of solution, even in the presence of 100-1000 times its amount of aluminum, 100 times its amount of Fe^{3+}, 300 times its amount of Mg^{2+}, and 700 times its amount of Ca^{2+}.

SUMMARY

1. It has been shown that chromotropic dyes give characteristic and very sensitive reactions with trivalent thallium. Univalent thallium salts do not give these reactions.

2. Some of the reagents tested permit determination of trivalent thallium salts without preliminary isolation in the presence of a large excess of certain other cations.

The reactions described for thallium can be used for the colorimetric determination of small amounts of thallium.

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POLAROGRAPHIC DETERMINATION OF ACRYLONITRILE
IN AQUEOUS-ALCOHOL SOLUTIONS

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The nitrile of acrylic acid is widely used as a basic raw material for the industrial production of various highly polymerized products. A rapid quantitative method of determining acrylonitrile is accordingly essential for the study and control of its polymerization processes.

The methods described in the literature — spectrophotometric [1], and spectroscopic [2] — for determination of acrylonitrile in solutions require special apparatus, which is not always available in an ordinary laboratory. The method of determining acrylonitrile by means of cyanoethylation is rather complicated [3].

Polarography has recently started to be used in industry for the quantitative determination of organic materials on a fairly wide scale. A visual apparatus for this purpose, can be assembled in any chemical laboratory by a suitable choice of resistances, as long as a sensitive enough galvonometer is available. The work described in the present article is devoted to the application of a polarographic method for the determination of acrylonitrile in aqueous solutions.

A method has been published for the polarographic determination of acrylonitrile [4], but the relation between diffusion current and concentration was not studied over a wide enough range by the authors (from only 13-3 mm/liter). Accordingly we studied this relation over a wider concentration range (approximately the range found during production control of polymerization processes); in addition, we studied the mechanism of the reduction of acrylonitrile on a dropping mercury electrode.

TABLE 1

Concentration of acrylonitrile in mM/liter	Wave height in μA	Diffusion current constant $I_d = \dfrac{i_d}{m^{2/3}t^{1/6}c}$
12,04	33,01	3,42
6,02	16,45	3,41
3,01	8,35	3,47
1,50	3,90	3,25
0,75	1,82	3,03
0,375	1,00	3,32
Mean value		3,31

EXPERIMENTAL

Work was carried out on a visual polarograph assembled in the laboratory on the usual principle.

The parameters of the M 21/1 galvanometer used were: $R_{VN} = 780\Omega$; $R_{KR} = 68,000\Omega$; the intensity of the galvanometer with respect to current was $0.664 \cdot 10^{-10}$ A/mm of the scale at a distance of 1.5 meters; the capillary characteristic was: $L = 1.25 \ mg^{2/3} \ sec^{-1/2}$ at zero potential. The supporting electrolyte consisted of 0.01 M $(C_2H_5)_4NCl$ in 1 liter of 50% ethyl alcohol, since, as was shown experimentally, it is necessary to use aqueous-alcohol mixtures for determination of acrylonitrile. The residual current in this electrolytic solution did not exceed 0.3-0.5 μA. A layer of mercury at the bottom of the electrolyzer served as anode, its potential on being measured with respect to a calomel electrode was found to be equal to +0.033 V.

In order to construct a calibration curve, solutions of acrylonitrile were prepared in which the concentration of the latter was varied from 12.04 to 0.3 mM/liter in the supporting electrolyte described above. The acrylonitrile was freshly distilled, and had a boiling point of 77°.

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POLAROGRAPHIC DETERMINATION ON SOLID ELECTRODES OF HEAVY METALS IN THE AIR OF INDUSTRIAL ESTABLISHMENTS

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During recent years Soviet scientists have developed a number of theoretical propositions in the field of polarography on solid electrodes.

The work of Skobets and others [1-7], has demonstrated the possibility of a practical application of solid electrodes in analytical practice. The advantages of solid electrodes over the dropping mercury electrode, and also the potential use of solid electrodes in anodic polarography have enabled quantitative determinations of small amounts of harmful materials to be carried out.

Our work was carried out on a "Geological prospecting polarograph" with automatic recording of I-V curves. The solid micro-cathode was made from platinum wire fused into a glass tube. A drop of silver was welded onto the platinum wire. A silver plate served as anode. The cathode was fixed in a metal tube, fitted in its turn into two ball bearings. The micro-cathode was rotated by means of a synchronous motor; this ensured uniform rotation. The rotation rate was 700-750 revolutions/minute. For a given rotation rate of the electrode, a limiting diffusion current was obtained as well as instantaneous stabilization of the current with time on the rotating electrode. The silver electrodes were amalgamated before each test by immersion in pure mercury.

Determination of Cadmium Oxide in the Air

Determination of cadmium oxide which one meets in non-ferrous metallurgy, smelting of zinc, etc. is of interest in industrial hygiene chemistry. The limiting permissible amount of cadmium oxide is 0.0001 mg/liter of air. Analysis of cadmium salts was carried out using 0.2 N ammonia as supporting electrolyte. Oxygen was removed from solution by addition of 0.2 g of sodium sulfite. Amalgamated silver plate 2 cm^2 in area served as anode. Known amounts of cadmium chloride were introduced into the electrolyzer, supporting electrolyte added, followed by 0.2 g of sodium sulfite. After 10 minutes the amalgamated electrodes were immersed in the solution, the cathode rotated at a rate of 700-750 revolutions/minute, and polarograms taken. All measurements were carried out with a galvanometer sensitivity of 1/5. On Fig. 1 are shown polarograms for solutions of varying concentrations of cadmium chloride using a rotating amalgamated silver cathode.

The half-wave potential of cadmium in a supporting electrolyte of 0.2 NH_4O was 0.51 V (with respect to the saturated calomel electrode). The tests carried out showed that reproducible results can be obtained (Table 1).

The aerosol of cadmium oxide was sampled into a five-liter evacuated flask. The air sample was treated with 0.2 N HNO_3 and left to stand for 20 minutes with frequent shaking. The contents of the bottle were transferred to a porcelain basin; the flask was rinsed 2-3 times
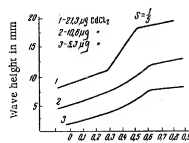
Fig. 1. Polarogram of cadmium chloride in a supporting electrolyte of 0.2 N ammonia.

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Fig. 2. Polarograms of copper and zinc when both are simultaneously present.

TABLE 1

Determination of Cadmium on a Rotating Solid Electrode

Cadmium taken in µg	Cadmium found in µg	% Determined
10,65	12,5	117
2	2	100
21,32	21,0	98
5,32	5,5	103

with 5 ml of water and the whole evaporated to dryness. The dry residue was treated 3 times with distilled water, evaporation to dryness being carried out after each treatment. The dry residue was finally treated with ammonia solution and transferred to the electrolyzer. The minimum amount of cadmium that could be determined amounted to 2 µg; the accuracy of the method is 5-10%.

Separate Determination of Zinc and Copper Oxides in Air

Separate determination of zinc and copper oxides in air presents a number of difficulties. Determination of zinc oxide has been studied by many authors [8, 9]. The half-wave potential of zinc is 1,2 V, while that of copper is 0.4 V (relative to the saturated calomel electrode) when the supporting electrolyte is ammonia. This fact, undoubtedly, plays a decisive part in the determination of the cations indicated when both are simultaneously present in the air. Tests were carried out with solutions of $CuSO_4$ in 0.2 N ammonia as supporting electrolyte. On Fig. 2 are shown polarograms of Cu^{2+} and Zn^{2+} when they were determined simultaneously. In order to carry out quantitative determinations of Cu^{2+} and Zn^{2+}, calibration curves were drawn for each cation in solutions of their respective salts, and test concentrations determined by means of these curves. Table 2 contains the results for separate determination of Cu^{2+} and Zn^{2+} on a solid electrode at a galvanometer sensitivity S = 1/5. Polarograms were taken by means of the method described above for cadmium oxide.

TABLE 2

Separate Determination of Cu^{2+} and Zn^{2+} on a Solid Rotating Cathode

Taken in µg		Found in µg		% Determined		Taken in µg		Found in µg		% Determined	
Cu²⁺	Zn²⁺	Cu²⁺	Zn²⁺	Cu²⁺	Zn²⁺	Cu²⁺	Zn²⁺	Cu²⁺	Zn²⁺	Cu²⁺	Zn²⁺
12	18	12	17,5	100	97	5	3	5	3	100	100
8	12	7,5	12,5	94	104	5	10	10	10	90	100
10	10	10	10	100	100	12	18	12	17,6	100	98

Determination of Manganese in Air

Manganese and its salts are widely used in machine construction, metal working, the mining industry, etc. The permissible limit for the concentration of manganese in air is 0.0003 mg/liter according to NSP-101-51. Manganese has been determined polarographically by a few authors [10-12]. In order to increase the sensitivity of the method, we made some tests on the behavior of manganese on a solid rotating drop-shaped silver electrode. Manganese was determined in a supporting electrolyte of 0.2 N KCNS. Hydrogen was passed through the solution for 10-15 minutes before taking polarograms. The total volume of the liquid being analyzed polarographically was 1.5 ml. The cathode was rotated at a speed of 800 revolutions/minute. Galvanometer sensitivity used was 1/20. The half-wave potential proved to be 1.5 V (with respect to the saturated calomel electrode). Solutions of $MnSO_4$ of varying concentrations were prepared in order to get a calibration curve.

Table 3 contains the results for polarographic determination of Mn in a supporting electrolyte of KCNS.

TABLE 3

Quantitative Determination of Manganese on a Solid Electrode

Taken in µg	Found in µg	% Determined	Taken in µg	Found in µg	% Determined
7	7	100	8	7,6	95
5	5	100	9	8,6	95
10	10,1	101	8	8,6	95
4	4	100	3	2,5	83
			6	6,5	108

Manganese in the air was trapped in a dust tube filled with hygroscopic cotton wool; the latter was given a preliminary treatment with 5% HNO_3, carefully washed with water to a neutral reaction with litmus, and dried in a drying oven. After taking test air samples, the cotton wool was removed from the tube, placed in a porcelain crucible and ignited in the crucible over a small flame of an alcohol burner. The residue was calcined at 600° in a muffle. The ash was dissolved in 1 ml of concentrated HNO_3 (sp. gr. 1.4), and the solution evaporated to dryness on a water bath. 5 ml of distilled water was added to the residue and the whole re-evaporated to dryness. This operation was repeated until the residue was neutral. The clear neutral solution was transferred from the crucible to the electrolyzer, and polarograms were taken by the method described above.

If a manganese content of more than 5 µg per liter of air is expected, samples can be taken in an evacuated 5 liter flask. Absorption of manganese is effected by 5 ml of HNO_3; subsequent procedure is then the same as that described above. The method developed for manganese determinations is simple and convenient. The sensitivity of the method is 1-2 µg of manganese in 1.5 ml of solution; the accuracy of the method is 10%.

Quantitative Determination of Chromates in Air

Chromates have found wide application in machine construction, the airplane, leather, textile, dye, and other industries.

The permissible limit of chromic anhydride, chromates, and dichromates is equal to 0.0001 mg/liter (the norm for planning industrial enterprises, NSP 101-51).

Our problem was to develop a sensitive method for determining chromates in the air of industrial enterprises.

Reduction of chromate ions on the dropping mercury electrode has been studied by Lingane and Kolthoff [13-14]. They assume that reduction proceeds as follows:

$$CrO_4^{2-} + 4H_2O + 3e \rightarrow Cr(OH)_3 + 5OH^-$$

$$CrO_4^{2-} + 2H_2O + 3e \rightarrow CrO_2 + 4OH^-.$$
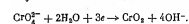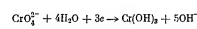
The reaction occurs in alkaline media. In neutral and non-buffered solutions, the polarogram for chromate consists of several waves.

We studied the behavior of chromate ions on solid amalgamated silver electrodes. Well-defined waves were obtained in a supporting electrolyte of 0.1-1N NaOH. On Fig. 3 are shown the characteristic waves obtained for chromate ions.

In order to determine chromate quantitatively, an aliquot of potassium chromate was dissolved in water. To the aqueous chromate solution was added 0.1 N NaOH. The total amount of the liquid to be polarographed was 2 ml. Sodium sulfite (0.2 g) was added to the alkaline chromate solution in the electrolyzer, and after 10 minutes polarograms were taken.
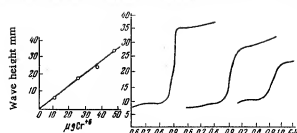
Fig. 3. Polarograms for chromate ions in 0.1 N NaOH as supporting electrolyte.
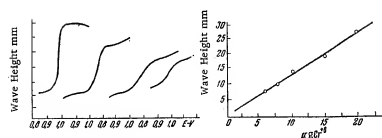
Fig. 4. Polarograms and calibration curve for CrO₃.

Determination was carried out on the basis of the reduction wave for Cr^{VI}. Electrolytic reduction of chromium from an alkaline solution of chromate gives a well-defined wave at a potential within the limits of 0.9-1.0 V.

Positive results were not obtained on taking polarograms of chromate ions in acid solutions; the reduction potential of the chromate ion is displaced to more negative values, and the chromate wave fuses with that of hydrogen. A calibration curve constructed for chromate in a supporting electrolyte of 0.1 N sodium hydroxide, in the presence of sulfite, shows a linear relationship between diffusion current and chromium concentration in solution (Fig. 3).

Similar results were obtained for chromium determinations in dichromate solutions. The Cr^{VI} wave is well defined in dichromate solutions. The chromium wave in an alkaline solution of dichromate, as well as the calibration curve, are similar to those for chromate solutions. Chromium anhydride (CrO_3) is widely used in electrolytic chrome plating; we studied the possibility of determining it quantitatively, on a solid amalgamated silver electrode. Tests were carried out in 0.1 N NaOH as supporting electrolyte, in presence of Na_2SO_3. Polarograms were taken under the conditions used for chromate and dichromate. The calibration curve was made with recrystallized CrO_3. Fig. 4 shows the calibration curve and polarograms for CrO_3.

Results for the polarographic determination of chromium in solutions of chromic anhydride are given in Table 4.

Aerosols of chromic acid and its salts can be trapped from the air in a dust tube, consisting of two cylindrical tubes. The inner tube is connected via a ground glass joint to the outer one. Filter paper is fitted to the end of the inner tube. Two samples are taken at each sampling point. 50-100 liters of air are sucked at the rate of 5-10 liter/minute using a vacuum pump and rheometer.

After sample taking, the filter paper was removed from the tube and placed in a porcelain basin. The tube was washed with a few portions of hot distilled water, this water being added to the basin containing the filter paper. The liquid was transferred to another basin. This operation was repeated 3-4 times. The liquid was then

TABLE 4

Results for the Polarographic Determination of CrO₃

Taken in μg	Found in μg	% Determined
34.46	37.5	108
27.5	26.25	95
24.1	27.5	114
20.8	22.5	108
13.78	15.75	114

evaporated on a water bath to 3-4 ml. It was poured from this basin into a cylinder, the basin was washed with hot water and the washings added to the same cylinder. 1 ml of test liquid was used for polarographic measurements; the procedure employed was the same as that described above.

SUMMARY

1. Polarographic analysis of small concentrations of heavy metals in air can be successfully carried out on solid rotating silver amalgamated cathode and anode.

2. Methods have been developed for the quantitative determination of Cu^{2+} and Zn^{2+}, Cd^{2+} and Mn^{2+} in air.

3. A method has been developed for the separate determination of Cu^{2+} and Zn^{2+} in air when they are simultaneously present.

4. A polarographic method for determining chromates in air has been developed.

5. The sensitivity of the methods developed amounts to 1-2 μg in 2 ml of liquid (the accuracy of the method is 10-15 %).

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KINETIC METHODS OF QUANTITATIVE ANALYSIS

PART III. DETERMINATION OF SMALL AMOUNTS OF MOLYBDENUM*

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The reaction $H_2O_2 + 2I^- + 2H^+ = 2H_2O + I_2^-$ only proceeds slowly at room temperature, and in the absence of catalysts. Some research workers [1, 2], have established that it obeys the bimolecular rule; its rate depends also on hydrogen ion concentration and foreign neutral salts. The presence in solution of very small amounts of molybdenum, tungsten, iron, vanadium, and other materials which can combine with hydrogen peroxide, speed up this reaction considerably [3, 4]; it has accordingly been used by us for developing a method for determining small amounts of molybdenum.

EXPERIMENTAL

The stock solutions used were: 0.01 M H_2O_2, 0.01 M KI, 4M H_2SO_4, starch solution, and a solution of ammonium molybdate containing 0.87×10^{-6} g/ml of Mo. The solutions of hydrogen peroxide, sulfuric acid, and starch were prepared from chemically pure materials. The potassium iodide was twice recrystallized from alcohol. The purity of the stock solutions was checked by measuring the reaction velocity under conditions described in the literature [2]. The fact that identical results were obtained testified to the absence of any appreciable amount of catalyzing impurities. The ammonium molybdate was analyzed by calcining at 300-400° and weighing the residue to MoO_3.

Into a 50 ml standard flask were introduced solutions of potassium iodide, sulfuric acid, water, and starch (the purity of the KI was once again established during this procedure), followed by the hydrogen peroxide and ammonium molybdate solutions. The mixture thus prepared was made up to the mark with distilled water and carefully mixed. The concentrations of the reactants in the flask after mixing were as follows: KI-0.0002 M, H_2SO_4-0.08 M, H_2O_2-0.001 M, ammonium molybdate (calculated as molybdenum) from $1.7 \cdot 10^{-8}$ g/ml to $8.7 \cdot 10^{-8}$ g/ml.

The solution was placed in the cell of an FM photometer, and 3 minutes after mixing, optical density was measured every minute using a N5 light filter (effective wave-length 553 mμ). On the basis of results obtained graphs were constructed of time — optical density; tangent of each line characterizing the reaction velocity of iodide oxidation was then determined (Fig. 1). All experiments were carried out at a temperature of 20-21°. During observation time not more than 6% KI and 1% H_2O_2 reacted. A curve was constructed of Mo concentration (tangent of the straight line); all points on this curve fall on one straight line (Fig. 2).

In order to find out the effect of acidity on the rate of the reaction being studied, various amounts of sulfuric acid were added to a reaction mixture consisting of $2 \cdot 10^{-4}$ mol/liter of KI, 10^{-3} mol/liter of H_2O_2 and $6 \cdot 10^{-7}$ mol/liter of molybdate. The relation between reaction velocity and amounts of sulfuric acid is shown in Fig. 3.

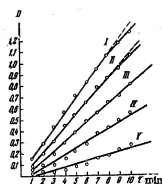* Part II. J. Anal. Chem. 10, No. 6, p. 344 (1955).

Fig. 1. Change of optical density in the system H_2O_2-KI-$(NH_4)_2MoO_4$.
Molybdate concentration in terms of molybdenum:
I) $8 \cdot 10^{-8}$ g/ml; II) $6 \cdot 10^{-8}$ g/ml; III) $4.3 \cdot 10^{-8}$ g/ml;
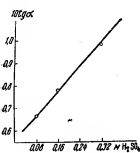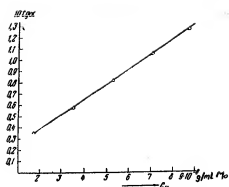IV) $2.4 \cdot 10^{-8}$ g/ml; V) $2.4 \cdot 10^{-8}$ g/ml.

Fig. 2. Relation between reaction velocity (1) and molybdenum concentration.

TABLE 1

Determination of Molybdenum on the Basis of Kinetic Results

Molybdate concentration in mol/liter	Molybdate found in mol/liter	Deviation in %
$4.86 \cdot 10^{-7}$	$4.48 \cdot 10^{-7}$	— 7.8
$4.50 \cdot 10^{-7}$	$4.80 \cdot 10^{-7}$	+ 6.7
$2.96 \cdot 10^{-7}$	$3.19 \cdot 10^{-7}$	+ 7.8
$1.91 \cdot 10^{-7}$	$1.89 \cdot 10^{-7}$	— 1.0

Fig. 3. Relation between reaction velocity (1) and H_2SO_4 concentration.

The results obtained are shown in Table 1

Finally, in order to determine the effect of various impurities on the accuracy of determination of molybdenum, various salts in concentrations ranging from $1.6 \cdot 10^{-4}$ M to $8.2 \cdot 10^{-4}$ M were added to test solutions (H_3PO_4 was used at a concentration of 10^{-2} M). Under these conditions, the concentration of test ion exceeded that of molybdenum by a few hundred times (from 250 to 1300 times as much). The results obtained are given in Table 2.

Four solutions were prepared each containing different amounts of ammonium molybdate; the amount of molybdenum was then determined in these solutions by measuring the reaction rate of iodide oxidation by hydrogen peroxide and using graph 2.

DISCUSSION OF RESULTS

The reaction rate of hydrogen peroxide with iodide in an acid medium, in the presence of molybdate, can be expressed to a first approximation, by the following equation:

$$\frac{d[I_2]}{dt} = \kappa c_{Mo} c_{H_2O_2} c_{I^-} , \qquad (1)$$

where κ is the catalytic coefficient, c_{H_2O}, c_{I^-}, and c_{Mo}, respectively, are the concentrations of hydrogen peroxide, iodide, and molybdate. It is possible that in acid media, molybdate may be partially converted into MoO_2^{2+} and other forms.

TABLE 2

Effect of Other Materials on Molybdenum Determination
(Concentration $6 \cdot 10^{-7}$ mol/liter Mo)

Other ion	Concentration of other ion in mM/liter	Ratio of concentration of other ion to molybdenum concentration	Tangent of the straight line t-D	Other ion	Concentration of other ion in mM/liter	Ratio of concentration of other ion to molybdenum concentration	Tangent of the straight line t-D
Co²⁺	0.94	570	$0.84 \cdot 10^{-1}$	Cr³⁺	0.38	630	$0.88 \cdot 10^{-1}$
Ni²⁺	0.34	570	$0.80 \cdot 10^{-1}$	Cd²⁺	0.16	250	$0.58 \cdot 10^{-1}$
Cu²⁺	0.31	520	$0.80 \cdot 10^{-1}$	Hg²⁺	0.50	830	$0.30 \cdot 10^{-1}$
Ca²⁺	0.50	830	$0.84 \cdot 10^{-1}$	VO₃⁻	0.20	330	$1.03 \cdot 10^{-1}$
Mg²⁺	0.82	1330	$0.84 \cdot 10^{-1}$	H₃AsO₄⁻	0.27	450	$0.00 \cdot 10^{-1}$
Mn²⁺	0.38	630	$0.84 \cdot 10^{-1}$	Silicate	1.0	—	$0.00 \cdot 10^{-1}$
Zn²⁺	0.31	520	$0.84 \cdot 10^{-1}$	H₃PO₄⁻	5.0	—	$0.70 \cdot 10^{-1}$

Actually, as is evident from the graphs adduced, the relation between reaction velocity and molybdenum concentration is somewhat more complicated and is better expressed by the equation:

$$\frac{d[I_2]}{dt} = \kappa c_{Mo} c_{H_2O_2} c_I + const. \qquad (2)$$

The value of the constant in equation (2) is not large. The catalytic coefficient as determined from equation (1) is equal to $1.4 \cdot 10^8$ (time in minutes, concentration in moles/liter).

On the basis of theoretical considerations which we advanced in our first paper [5], it is possible to estimate the minimum concentration of molybdenum which can be detected by this method. For this purpose it is necessary to know the velocity constant for the non-catalyzed reaction. Under our conditions this value, according to published results, would be equal to 3.68, from which:

$$c_{Mo_{min}} \approx 0.1 \frac{k}{\kappa} = 2.6 \cdot 10^{-9} \text{ M}. \qquad (3)$$

Consequently, the method which we have suggested is far more sensitive than any method hitherto known for determining molybdenum.

The experiments described here for molybdenum determination were carried out at higher concentrations (from $1.8 \cdot 10^{-7}$ M to $9.1 \cdot 10^{-7}$ M); this corresponds to a range of from 0.17 to 0.87 μg per 10 ml. These concentrations are also considerably lower than those used for colorimetric analysis. In this molybdenum concentration range, reproducibility is 10%. When the method described here (for determinating molybdenum concentrations) is used, there is no need to introduce corrections for the velocity of the non-catalyzed reaction; this simplifies the analytical method appreciably.

Experiments which we carried out demonstrated the possibility of determining molybdenum at even lower concentrations; however, the reproducibility drops off significantly. This is connected with the fact that at very low molybdenum concentrations, impurities play a very essential role — complete freedom from silicate is impossible when glass apparatus is used. Presumably, lower concentrations could be handled if the effect of silicate could be completely eliminated.

The reaction rate of oxidation of iodide by hydrogen peroxide depends on hydrogen ion concentration. With increasing acid concentration in solution, reaction rate increases. It is possible that in the given instance, formation of the hydroperoxonium ion $H_3O_2^+$, which reacts more vigorously with iodide, occurs.

Determination of molybdenum by the method suggested is possible in the presence of many other metals. Cobalt, nickel, copper, calcium, magnesium, manganese, zinc, chromium (trivalent) have no significant effect on reaction velocity at the concentrations studied. In the presence of vanadate there is an appreciable increase in reaction rate; this, apparently, can be explained by the formation of a complex between vanadate and hydrogen peroxide. Reaction rate also increases in the presence of tungstate. Materials which oxidize iodide should also be absent. Slowing down of the reaction by mercury and cadmium ions is related to the fact that these elements form complexes with iodide and lead to a sharp decrease in its concentration. Phosphate slows down the reaction; in the presence of silicate and arsenate, in general, no evolution of iodine is observed. All these ions form complexes with molybdate and suppress its catalytic activity sharply.

The practical absence of oxidation of iodide by hydrogen peroxide in dilute solutions, in the presence of molybdate and silicate or arsenate can be used for detection of these two latter ions in qualitative analysis. It is possible in this way to detect very small amounts of arsenate and silicate.

SUMMARY

A new method is suggested for the determination of small amounts of molybdenum; it is based on making use of the catalytic effect of molybdate on the oxidation of iodide by hydrogen peroxide. The method has been checked in the concentration range $1.8 \cdot 10^{-7}$ to $9.1 \cdot 10^{-7}$ M.

The effect of other materials on the accuracy of determination has been studied.

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* T. p. = Consultants Bureau Translation pagination.

CEMENTATION OF CERTAIN METALS BY ZINC AMALGAM

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In recent years interest in developing amalgam methods of quantitative separation and determination of metals has increased, as well as the search for amalgam methods suitable for hydrometallurgical treatment of poor ores with the aim of using their components.

As Hohn [1], has pointed out, the method of amalgam metallurgy is particularly important for treating poor ores.

One of the fundamental stages in amalgam metallurgy is cementation (phase exchange) with amalgams. Without dwelling on the theory of the cementation process, which has been discussed in detail in a series of papers by Kozlovsky and coworkers [8, 9], we note that for the purposes of cementation, the most suitable amalgams are those of the metals: zinc, cadmium, tin, lead, and bismuth. These metals dissolve readily in mercury without reacting chemically with it; as a result, their deposition potentials on mercury do not differ from their deposition potentials on solid cathodes. The most active amalgam of the group of metal amalgams indicated, is that of zinc. Zinc amalgam has been used by many authors [2-4], for quantitative separation of metals, and for cementation of metals which interfere with the determination of anions in sparingly soluble and complex salts, for determination of metals by the method of internal electrolysis [5], and also in volumetric analysis as a reducing agent [6, 7].

It should be noted however, that no systematic studies have been carried out on the cementing capacity of zinc amalgam as applied to certain metals.

In the investigation described in the present article we studied cementation of copper, cadmium, lead, antimony, nickel and iron by zinc amalgam, as follows:

A. The quantitative ratios of the cathode-reducing metals to anode-oxidizing zinc were determined.

B. The effect of concentration and electrolyte composition on the rate of the process was established, and the percentage efficiency of the zinc determined.

Cementation was carried out in solutions of sulfuric and hydrochloric acids, and in ammonia solution.

In the first series (a) of experiments, 0.1 M solutions of the acids indicated and 0.1-1 M ammonia solutions were used. Concentrations of the zinc amalgam were varied within the limits 2 to 7%.

In the second series (b), the amalgam concentration was kept constant (2%), while the concentration of electrolyte was changed (0.01-1 M).

The first series of experiments were carried out by shaking a solution containing the metals to be cemented in amounts equivalent to the zinc, in a separating funnel. Completness of deposition of the metals was controlled by using the appropriate qualitative reactions for the various metals: copper – potassium ferrocyanide, lead – sodium sulfide, cadmium – sodium sulfide, antimony – hydrogen sulfide, nickel – dimethylglyoxime, and iron – potassium ferricyanide.

The second series of tests was carried out in the apparatus shown schematically in Fig. 1. In the vessel was placed 70 ml of solution, containing in all cases 0.05 g of the cemented metal in hydrochloric, sulfuric or ammonia of a definite concentration, and then amalgam introduced. Cementation was effected by stirring the amalgam and solution with a glass stirrer in a hydrogen atmosphere. The stirrer was rotated at a speed of 400 revolutions/minute.

Cementation stopped after 15 minutes. The solution was separated from the amalgam and analyzed for its content of cemented metal and zinc; on this basis, calculations were made of the amount of cemented metal which had transferred to the amalgam, and also of the percentage efficiency of the zinc (the amount of zinc consumed).

In some experiments (Series a) measurement of the potential during cementation was carried out by means of the usual compensation method. For this purpose the apparatus shown in Fig. 1 was used. The reference electrode was a saturated calomel electrode.

On the basis of the ratios of the half-wave potentials of the metals subjected to reduction from their simple and complex salts, to the potentials of the zinc amalgam it is possible to predict that copper, cadmium, lead, and antimony will be cemented from any solution, nickel only from ammonia solution, while iron will not be cemented at all by zinc amalgam.

Experimental results (Table 1) showed that copper, cadmium, and antimony are actually cemented from any solutions; nickel is cemented only when ammonia is used as supporting electrolyte, and iron is not cemented. Lead, despite expectations, is not cemented from sulfuric acid through the potential of lead, calculated on the basis of the solubility product of lead sulfate ($2 \cdot 10^{-8}$), proves to be more positive than the potential of the zinc amalgam. This divergence between theoretical assumptions and practice can apparently be explained by the low rate of the process of solution of lead sulfate.
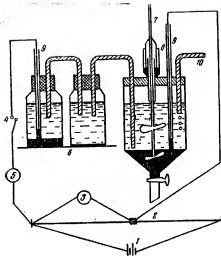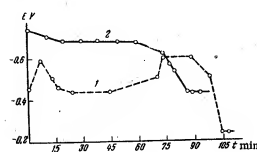

Fig. 1. Schematic diagram of the apparatus for metal cementation.
1) Accumulator; 2) rheocord; 3) voltmeter; 4) key; 5) galvanometer; 6) half-element; 7) stirrer; 8) mercury seal; 9) contacts; 10) tube for hydrogen.

Fig. 2. Change in potential of the amalgam during cementation of lead and cadmium:
1) for Pb; 2) for Cd.

It was noted that during cementation of copper, nickel, lead, and cadmium in solutions of ammonia of low concentrations, black precipitates are formed, while drops of broken up amalgam loose their capacity to fuse into each other. These precipitates, according to spectrographic analysis, contain the reduced metals and finely broken up mercury. With increasing ammonia concentration, the amount of black precipitate decreases. This observation can be explained as follows: at low ammonia concentrations the potential of the amalgam becomes more positive. With the shift in potential to more positive values, the surface tension of the mercury increases, thanks to which, penetration of the metals into the mercury becomes more difficult. For the same reason zinc only dissolves in mercury with difficulty in the absence of electrolyte. The presence of any electrolyte shifts the potential of the amalgam to more negative values, and at the same time depresses the surface tension of the mercury.

TABLE 1

Cementation of Metals by Zinc Amalgam in Various Media

Concentration of Zn in the amalgam in %	Metal	Supporting electrolyte				Observations
		0.1 M HCl	0.1 M H₂SO₄	0.1 M NH₄OH	1 M NH₄OH	
2	Cu	+	+	+	+	With increasing ammonia concentration, the amount of metal passing into the amalgam increases
3	»	+	+	+	+	
5	Cd	+	+	+	+	
2	»	+	+	0	0	
3	»	⊕	⊕	0	0	
5	»	⊕	⊕	0	0	
2	Pb	⊕	—	0	0	
3	»	⊕	—	0	0	
7	Ni	—	—	~	~	
2	»	—	—	~	~	
3	Sb	Δ	Δ	Δ	Δ	
3						

Arbitrary Designations: ⊕) Metal is cemented in equivalent amounts with respect to zinc; +) cementation with formation of intermetallic compound; 0) cemented in equivalent amounts, but does not transfer quantitatively into the amalgam; Δ) cemented without formation of amalgam; ~) cemented, but not in equivalent amounts and does not transfer quantitatively into the amalgam.

TABLE 2

Cementation of Copper by Zinc Amalgam
Concentration of Supporting Electrolyte 0.1 M/Liter; Amount of Amalgam 100 g

Electrolyte	Concentration of Zn in the amalgam in %	Amount of Cu in g in the solution before commencement of cementation	Amount of Cu in g remaining in solution after cementation	Amount of Zn in g which goes into the amalgam during cementation	Amount of Cu in g which goes into the amalgam	Amount of Zn in g remaining in the amalgam	Potential at the beginning of the process	Potential of the amalgam at the end of the process	Atomic relation of zinc and copper in the amalgam	Time spent on cementation (or after drop in potential) (in hours)
HCl	1	2.2905	1.9665	0.3486	0.3240	0.6514	−0.74	+0.21	2 : 1	—
HCl	1	2.3095	1.8954	0.4727	0.4642	0.5273	−0.74	+0.21	1.1 : 1	1
HCl	1	2.3095	—	—	—	—	−0.74	+0.31	1 : 1	—
HCl	2	2.3095	1.6680	0.6316	0.6415	1.3580	−0.74	+0.21	2.01 : 1	—
HCl	2	2.3095	1.4092	0.8796	0.9003	1.1204	−0.74	+0.21	1.2 : 1	15
HCl	2	2.3095	1.3435	0.9956	0.9660	1.0440	−0.74	+0.31	1 : 1	—
HCl	2	2.3095	1.2034	1.1842	1.0872	1.1842	−0.74	+0.31	1 : 1	11
HCl	2	2.3095	1.0646	1.2685	1.2449	2.7315	−0.85	+0.21	2 : 1	—
HCl	4	2.3095	0.7224	1.5883	1.5871	3.417	−0.77	+0.21	2 : 1	—
HCl	5	2.3095	0.7210	1.7100	0.6790	1.2900	−0.91	−0.08	1.9 : 1	—
NH₄OH	2	2.2905	1.4493	0.9686	0.7712	1.0314	−0.89	−0.16	1.3 : 1	13
NH₄OH	2	2.405	1.5130	1.2107	0.8870	0.7893	−0.91	−0.01	0.87 : 1	3 min.
NaOH	2	2.2905	1.6300	0.6818	0.6605	1.3682	−1.19	−0.55	1.94 : 1	—
NaOH	2	2.2905	1.3855	0.9337	0.9055	1.0663	−1.19	−0.25	1 : 1	—

Measurements of the potentials of the amalgam during cementation in hydrochloric acid solutions show that, in the case of cadmium (Fig. 3, Curve 2), the potential of the amalgam changes from the potential of zinc (at the start of the process) to that of cadmium (at the end of the process). The amount of cadmium reduced is equivalent to the amount of zinc. The change in potential of the amalgam is shown in Fig. 2 (Curve 1). Lead is also cemented in amounts equivalent to those of zinc.

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Concentration of Zn in the amalgam in %	Metal	Supporting electrolyte				Observations
		0.1 M HCl	0.1 M H_2SO_4	0.1 M NH_4OH	1 M NH_4OH	
2	Cu	+	+	+	+	With increasing ammonia concentration, the amount of metal passing into the amalgam increases
3	»	+	+	+	+	
5	»	+	+	+	+	
2	Cd	+	+	⊕	⊕	
3	»	⊕	⊕	0	0	
5	»	⊕	⊕	0	0	
2	Pb	⊕	—	0	0	
3	»	⊕	—	0	0	
5	»	⊕	—	0	0	
2	Ni	—	—	~	~	
7	»	—	—	~	~	
3	Sb	△	△	△	△	

Arbitrary Designations: ⊕) Metal is cemented in equivalent amounts with respect to zinc; +) cementation with formation of intermetallic compound; 0) cemented in equivalent amounts, but does not transfer quantitatively into the amalgam; △) cemented without formation of amalgam; ~) cemented, but not in equivalent amounts and does not transfer quantitatively into the amalgam.

TABLE 2

Cementation of Copper by Zinc Amalgam
Concentration of Supporting Electrolyte 0.1 M/Liter; Amount of Amalgam 100 g

Electrolyte	Concentration of Zn in the amalgam in %	Amount of Cu in g in the solution before cementation (mg-equiv/liter)	Amount of Cu in g remaining in solution after cementation	Amount of Zn in g which goes into solution during cementation	Amount of Cu in g which goes into the amalgam	Amount of Zn in g remaining in the amalgam	Potential at the beginning of the process	Potential of the amalgam at the end of the process	Atomic relation of zinc and copper in the amalgam	Time spent on cementation after drop in potential (in hours)
HCl	1	2,2905	1,9665	0.3486	0.3240	0.6514	—0.74	+0.21	2 : 1	—
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HCl	1	2,3095	—	—	—	—	—0.74	+0.31	1 : 1	—
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HCl	2	2,3095	1.2034	1.1842	1.0872	1.1842	—0.74	+0.21	2 : 1	11
HCl	4	2,3095	1.0646	1.2685	1.2449	2.7315	—0.85	+0.31	2 : 1	—
HCl	5	2,3095	0,7224	1.5883	1.5871	3 417	—0.77	+0.21	2 : 1	—
NH₄OH	2	2,2905	1.7210	0.7100	0.6790	1.2900	—0.91	—0.08	1,9 : 1	13
NH₄OH	2	2.2905	1.4493	0.9686	0.7712	1.0314	—0.89	—0.16	1.3 : 1	13
NH₄OH	2	2.405	1.5130	1.2107	0.8870	0.7893	—0.91	—0.01	0.87 : 1	3 min.
NaOH	2	2.2905	1.6300	0.8818	0.6605	1.3182	—1.19	—0.55	1.94 : 1	—
NaOH	2	2.2905	1.3855	0.9337	0.9055	1.0663	—1.19	—0.31	1 : 1	—

Measurements of the potentials of the amalgam during cementation in hydrochloric acid solutions show that, in the case of cadmium (Fig. 3, Curve 2), the potential of the amalgam changes from the potential of zinc (at the start of the process) to that of cadmium (at the end of the process). The amount of cadmium reduced is equivalent to the amount of zinc. The change in potential of the amalgam is shown in Fig. 2 (Curve 1). Lead is also cemented in amounts equivalent to those of zinc.
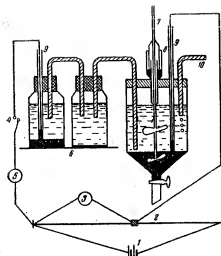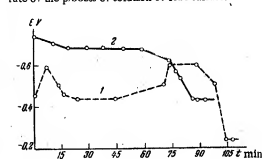
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We suggest that the variations in potential of the amalgam, which can be seen in the curve, are determined by the formation of a film of metallic lead on the amalgam surface: the rate at which lead dissolved is less than its cementation rate. In the case of copper, here the chemical interaction between copper and zinc in the amalgam obviously affects the character of the cementation process. During a certain time interval (in 0.1 M HCl) the amalgam potential corresponds to the zinc potential, while it subsequently changes rapidly to +0.21 V (Fig. 3, Curve 1). On using a more concentrated amalgam (4-5%) instead of the 2% amalgam, the same effect
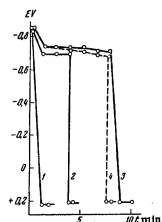

Fig. 3. Change in the potential of the amalgam during cementation of copper; 1) 1% amalgam; 2) 2% amalgam; 3) 3% amalgam; 4) 5% amalgam.
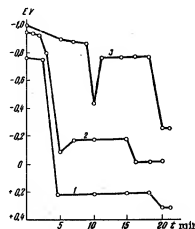
Fig. 4. Change in the potential of the amalgam during cementation of copper in various media: 1) 0.1 M HCl; 2) 0.1 M NH$_4$OH; 3) 0.1 M NaOH.

is observed, but with the difference that the potential jump occurs after a longer time interval, and the horizontal section of the curve increases. The potential jump to +0.21 occurs when there is still an appreciable amount of zinc left in the amalgam. By means of quantitative analysis we calculated the ratio of zinc to copper in the amalgam at the point where there is a sudden drop in potential. This ratio proved to be 2:1 (independently of the concentrations of the amalgam used). This seems to suggest formation of a compound with the composition Zn_2Cu in the amalgam.

A compound of the composition indicated has actually been found by Pushin [10], in copper-zinc alloys. Russel [11], detected it in amalgams using a totally different method — oxidation of amalgams with chemical reagents (KMnO$_4$ etc).

After the occurrence of the first potential jump, formation of a precipitate of cuprous chloride starts in solution. Subsequently, after a certain time interval, there is observed a second jump to +0.31 V (Fig. 4, Curve 1). The ratio of zinc to copper in the amalgam corresponding to this potential jump proved to be 1:1, which suggests the formation of a second compound of copper and zinc with the composition ZnCu. We suggest that the compound Zn_2Cu dissociates according to the equation:

$$Zn_2Cu \;\rightleftharpoons\; ZnCu + Zn,$$
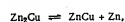
while the zinc formed as a result of this dissociation, immediately reacts as follows: $Zn + 2Cu^{2+} \rightleftharpoons Zn^{2+} + 2Cu^+$.

Further, metallic copper is formed according to the equation: $2Cu^+ \rightarrow Cu + Cu^{2+}$, this copper then goes into the amalgam and reacts with the compound found in the amalgam as follows:

$$Zn_2Cu + Cu \;\rightleftharpoons\; 2ZnCu$$
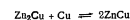
On further agitation, the reduction of copper by the zinc separating out from the compound does not stop either.

TABLE 3

Effect of Concentration of Supporting Electrolyte on the Rate of Cementation of Metals by Zinc Amalgam

Supporting electrolyte in M/liter	Metal	Amount			% Efficiency of zinc (i.e. amount usefully employed)
		Me, separated after 15 minutes	Zn used up in extracting the metal	Zn used for evolution of hydrogen	
HCl 0.01 / 0.1 / 1	Cu	0.032 / 0.036 / 0.037	0.032 / 0.037 / 0.039	0.006 / 0.006 / 0.009	84 / 86 / 79
H$_2$SO$_4$ 0.01 / 0.1 / 1		0.035 / 0.035 / 0.035	0.036 / 0.036 / 0.036	0.006 / 0.009 / 0.011	86 / 80 / 77
NH$_4$OH 0.01 / 0.1 / 1		0.006 / 0.040 / 0.038	0.005 / 0.0308 / 0.0387	0.015 / 0.0132 / 0.0063	25 / 70 / 88
HCl 0.01 / 0.1 / 1	Cd	0.023 / 0.025 / 0.030	0.013 / 0.013 / 0.017	— / — / —	100 / 100 / 100
H$_2$SO$_4$ 0.01 / 0.1 / 1		0.023 / 0.025 / 0.030	0.013 / 0.013 / 0.017	— / — / —	100 / 100 / 100
NH$_4$OH 0.01 / 0.1 / 1		0.005 / 0.016 / 0.022	0.003 / 0.009 / 0.013	0.001 / 0.001 / —	75 / 90 / 100
HCl 0.01 / 0.1 / 1		0.034 / 0.035 / 0.030	0.011 / 0.011 / 0.0094	0.006 / 0.006 / 0.0086	68 / 65 / 52
NH$_4$OH 0.01 / 0.1 / 1	Pb	0.008 / 0.027 / 0.017	0.0025 / 0.0085 / 0.0053	0.0025 / 0.0015 / 0.0047	50 / 85 / 53
HCl 0.01 / 0.1 / 1		0.031 / 0.036 / 0.035	0.017 / 0.019 / 0.019	0.032 / 0.090 / 0.228	34 / 18 / 7
H$_2$SO$_4$ 0.01 / 0.1 / 1	Sb	0.024 / 0.036 / 0.026	0.013 / 0.019 / 0.012	0.020 / 0.120 / 0.168	40 / 14 / 6
NH$_4$OH 0.01 / 0.1 / 1	Ni	Traces / 0.023 / 0.035	— / 0.025 / 0.039	— / 0.003 / —	— / 89 / 100

Experiments carried out in 0.1 N ammonia and alkali solutions respectively, showed (curves 2, 3, Fig. 4), that during cementation of copper under these conditions, two potential jumps are observed:

	Alkali supporting electrolyte	Ammonia supporting electrolyte
First jump	−0.55 V	−0.08 V
Second jump	−0.25 V	−0.01 V

In this case, after the first potential jump, there is a new shift to a negative value (this was not observed in hydrochloric acid media).

The ratio of copper to zinc corresponding to the first jump is 2:1, while for the second jump the ratio is 1:1. In alkali media, after the first jump, a precipitate of Cu_2O is formed, while in the ammoniacal media, the precipitate of Cu_2O dissolves to form the complex $(Cu/NH_3/_2)_2SO_4$.

By means of such investigational methods as anodic oxidation of amalgams, polarographic methods, titration of amalgam with mercury salts, we could not establish the presence of a copper-zinc compound with a zinc content greater than 50% (in terms of number of atoms) in the amalgam. It follows therefore that the cementation method, together with measurement of potential, may give a more complete picture of the chemical interactions between cemented and cementing metals in an amalgam.

The second series of experiments, as indicated above, were devoted to finding out the effect of electrolyte concentration on the rate of cementation and on the amount of zinc usefully employed. Results are given in Table 3.

The results obtained indicate that the nature and concentration of electrolyte has an effect both on the rate of the cementation process, and on the amount of zinc usefully employed. The process rate in acid solutions, exceeds, as a rule, the rate in ammonia solutions. Increasing the supporting electrolyte concentration speeds up the cementation process; this is the result of an increase in the electrical conductivity of the solution, and an increase in current of the local elements which follows from this.

The amount of zinc usefully employed decreases as the electrolyte concentration increases. An exception in this connection is cadmium, which it is known has a high hydrogen overvoltage. There is a particularly sharp drop in the percentage of zinc usefully employed in the case of antimony cementation.

SUMMARY

1. It has been demonstrated that it is possible to use zinc amalgam for the quantitative extraction of cadmium and antimony from hydrochloric, sulfuric, and ammonia solutions; lead — from hydrochloric and ammonia solutions; and nickel — from ammonia solutions, with subsequent formation of amalgam (exception Sb).

2. It has been established that for equivalent ratios of zinc in the amalgam and copper in solution, copper is not quantitatively extracted from solution by a zinc amalgam, because of the formation of chemical compounds Zn_2Cu and $ZnCu$. Definite potential jumps were found to correspond to the formation of the compounds indicated. Quantitative extraction of copper can be achieved by using a zinc amalgam, containing zinc in amounts which exceed the copper content of the solution by not less than 3 times this amount.

3. It has been shown that measurement of the potential of the amalgam cementation permits one to establish the presence of chemical compounds of the cemented and cementing metals respectively, in the amalgam at the moment when they are formed; this may prove to be an effective method for studying amalgams.

4. The effect of electrolyte concentration on the rate of the cementation process, and on the amount of zinc usefully employed has been studied.

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A MERCURIMETRIC METHOD OF DETERMINING IODIDES

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On addition of mercuric salts to an excess of iodide solution the complex ion HgI_4^{2-} is formed. On addition of more Hg^{2+} ions, as a result of the reaction

$$HgI_4^{2-} + Hg^{2+} \longrightarrow 2HgI_2,$$
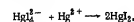
near the equivalence point, a yellow turbidity of HgI_2 appears, on shaking, the color changes to red. This reaction was first used for quantitative determination of iodides in 1832 by Morozeau [1]. Nevertheless, because of the necessity of introducing corrections for the appearance of the red turbidity before the equivalence point, the method has not been widely used. Stanek and Nemes [2], titrated iodides in the presence of sodium nitro-prusside which forms a turbidity with the Hg^{2+} ion at the equivalence point. Practice has shown that when sodium nitroprusside is used as the indicator, it is not possible to determine more than 20 mg of iodide in 200 ml of solution being titrated; otherwise the turbidity of HgI_2 which appears does not permit the titration end-point to be established.

Dubsky and Trtilek's method [3], is a more convenient mercurimetric method for determining low concentrations of iodides; they suggested titrating the test iodide solution with mercuric nitrate in an acid medium, in the presence of diphenylcarbazone which forms with Hg^{2+} a violet colored compound. Just as in the previous instance, however, titration of more concentrated iodide solution is rather difficult on account of precipitation of HgI_2 at the end-point. In order to increase the sensitivity of the indicator change, the authors were compelled to titrate in a standard flask until the appearance of a color which indicates that the reaction is coming rapidly to an end; at this point they added water, made the solution up to the mark, and filtered off the precipitate of HgI_2 formed; subsequently a known volume of the solution in the standard flask was titrated until the appearance of a red-violet color. It is quite understandable why Dubsky and Trtilek's method, despite the high sensitivity of the indicator, has not found wide practical application; it is the result of the complexity of operations and the difficulty in finding the end-point. The basic factor which complicates carrying out titration, in the given instance, is the appearance of the HgI_2 precipitate. This drawback can be eliminated by replacing water — the usual solvent — by another liquid in which the HgI_2 formed during the reaction is soluble. Experiments which we carried out showed that ethyl alcohol is capable of dissolving enough of the HgI_2; in addition, use of this solvent leads to an increase in sharpness of indicator change and enhances the sensitivity.

In order to determine the optimum titration conditions for iodides in an aqueous-alcohol medium, we titrated 0.01 N solution of potassium iodide with a solution of $Hg(NO_3)_2$ of roughly the same concentration in solvent mixtures containing different amounts of alcohol, and which are slightly acidified with nitric acid. A 1% alcohol solution of diphenylcarbazone was used as indicator. Results are given in Table 1.

Accordingly, the most suitable medium for working with 0.01 N solutions proved to be an aqueous alcohol one, consisting of 5 ml of 96° alcohol and 1 ml of test iodide solution. Under these conditions, the solution remains perfectly clear up to the end point, while the color change of the indicator is exceptionally sharp. Titration of iodides in a homogeneous medium does not require the introduction of any corrections.

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TABLE 1

Mercurimetric Titration of KI (1.243 mg I^-/ml) in Aqueous and Aqueous-Alcohol Media

Volume in ml		Amount of ~0.01 N Hg(NO₃)₂ used in ml	I^- found in mg	Error in %	Observations
Water	Alcohol				
5.0	0.0	1.140	1.236	−0.56	Lots of precipitate formed
4.0	1.0	1.140	1.236	−0.56	Indicator color change not sharp enough
3.0	2.0	1.140	1.236	−0.56	
2.0	3.0	1.142	1.238	0.40	Turbidity appears towards end of titration
0.0	5.0	1.146	1.243	0.00	Solution remains clear up to the end-point. Color change at end-point exceptionally sharp.

TABLE 2

Mercurimetric Determination of Small Amounts of I^- Ions in a Homogeneous Aqueous-Alcohol Medium

I taken in mg	I found in mg	Error in %	I taken in mg	I found in mg	Error in %
0.870	0.8706	+0.07	1.612	1.612	0.00
1.243	1.243	0.00	1.740	1.737	−0.11
1.491	1.491	0.00	1.864	1.859	−0.26
1.368	1.372	+0.29			

The following solutions are necessary for iodide determination: 1) 0.01 N Hg(NO₃)₂; 2) 1% alcohol solution of diphenylcarbazone (stable for weeks); 3) approximately 1 N HNO₃.

Standard Hg(NO₃)₂ of the concentration indicated is prepared from chemically pure mercuric oxide; for this purpose 1.09 g of HgO is moistened in a liter standard flask with a small amount of water, it is dissolved by addition of 1.5-2.0 ml of concentrated nitric acid. When the precipitate has dissolved completely the solution is made up to a liter with water and filtered. In the absence of mercuric oxide, the Hg(NO₃)₂ solution can be prepared by dissolving metallic mercury in HNO₃ [4].

The standard mercuric nitrate solution was standardized against 0.01 N KCl. For this purpose, to one 1 ml of KCl solution is added 5 ml of 96° alcohol free of halides, and two drops of the 1% alcoholic solution of diphenyl-carbazone; the solution is acidified with one or two drops of 1 N HNO₃ until the color which is formed on addition of the indicator disappears, and the whole titrated with Hg(NO₃)₂ from a micro-buret to the appearance of a weak violet-rose color.

Determination of iodide is carried out in excatly the same way as standardization of 0.01 N Hg(NO₃)₂. To 1 ml of test liquid containing approximately 0.13-0.15 g of iodide in 100 ml of solution is added 5.0 ml of 96° alcohol, 2 drops of the 1% alcoholic solution of diphenylcarbazone, 1-2 drops of nitric acid and the whole titrated with 0.01 Hg(NO₃)₂ to the appearance of a weak violet-rose color.

Table 3 contains some results for the determination of iodide in chemically pure preparations of lead iodide and potassium iodide.

In addition to studying the conditions for titrating iodides in dilute solution, we were also interested in the possibility of working with 0.1 N solutions. Experiments which we carried out showed that on addition of sufficient alcohol to the amount of working solution taken, such a method can be realized. Optimum conditions are achieved in such cases by adding to 1.0 ml of 0.1 N test solution, 10 ml of ethyl alcohol. When such a ratio of

TABLE 3

Test compound	Weight taken in mg	I content in %		Error in %
		Found	Theoretical	
PbI₂	0.3141	55.22	55.05	+0.17
PbI₂	0.3141	55.22	55.05	+0.17
KI	1.6260	76.35	76.45	−0.10
KI	1.6260	76.50	76.45	+0.08

the volume of solution to be titrated and alcohol (1:10) is used, the working solution remained clear to the end-point, and the indicator color change is exceptionally sharp.

For the determination of iodide in potassium iodide, 0.980 ml of 0.1 N Hg(NO₃)₂ was used to titrate 1.0 ml of solution to be titrated containing 16.257 mg of iodide; this corresponded to 76.47% I (theoretical content 76.45%). For titration we used, in all cases, a tapless pneumatic micro-buret, since we preferred this type to all other models of similar apparatus.

It should be pointed out in conclusion, that apart from its advantages over other mercurimetric methods proposed previously, this method can compete in accuracy with iodometric methods, since the sensitivity of diphenylcarbazone in alcohol media towards Hg²⁺ ions is several times higher than that of the iodine-starch reaction.

SUMMARY

A simple and convenient mercurimetric method has been developed for the determination of iodides by titration in aqueous-alcohol media. The method does not require any corrections and is distinguished by a high accuracy.

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A METHOD OF CONCENTRATING TRACES OF COPPER BY MEANS OF
ORGANIC REAGENTS

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We have shown [1], that quantitative concentration of traces of a metal (micro component) by partial precipitation of another metal (macro-component) as a basic salt, can only be achieved under such conditions that a known amount of the latter is precipitated; under these conditions, with changes in concentration of the micro-component metal, all other conditions being equal, the micro-component will be distributed between solution and precipitate in a constant ratio. It was also noted that during concentration of the method considered, practically complete separation of impurities, in the form of those metals which form more soluble compounds with the reagent than the macro-component metal, can be effected [2].

When 8-hydroxyquinoline which forms inner-complex compounds with metals is used as a reagent, different regularities were observed. If, for sufficiently high concentrations of the micro-component metal, the latter practically completely goes over into the precipitate, then on decreasing the concentration to a known limit, the amount of it which is caught in the precipitate will decrease sharply (Table 1). In addition, it was established that at a concentration of the micro-component near to this limit, the amount of it trapped in the precipitate decreases with increasing solution volume, and hardly changes at all with increasing macro-component concentration. In this connection, it was of interest to establish: a) the effect of a subsequent extraction of precipitate with a non-miscible solvent (after precipitation of part of the macro-component with an organic reagent) and b) the possibility of separating, during concentration in this way, impurities in the form of metals which form more soluble compounds (or less stable complexes) with the organic reagent than the macro-component metal does.

For solving the first problem we used 8-hydroxyquinoline as reagent, while for solving the second we used — diethyldithiocarbamate.

1. Concentration of Copper from a Solution of Lead Nitrate by Means of 8-Hydroxyquinoline

Investigation of concentration by means of 8-hydroxyquinoline was carried out as follows: to 8 ml of 0.1 M lead nitrate, purified from copper by precipitation with hydrogen sulfide [2], was added a solution of a copper salt, 1 ml of 2 M sodium acetate and 0.5 ml of 0.15 M 8-hydroxyquinoline solution (quinosol). The mixture was shaken for 5 minutes and then centrifuged, the precipitate was washed with 5 ml of distilled water and dissolved in 2 ml of 2N nitric acid. Copper was then determined in the solution thus obtained after adding sulfuric acid to it and making its volume up to 10-12 ml, by the dithizone method (by the method of mixed colors [3]). A blank run in exactly the same way, was used as a standard; in this case, copper was introduced into the nitric acid solution obtained after dissolving lead 8-hydroxyquinolate.

Using the same conditions, parallel experiments were carried out on concentration of copper by partial precipitation of lead as the 8-hydroxyquinolate, with subsequent extraction of the precipitate with chloroform. The 8-hydroxyquinolates were extracted with 5-6 lots of 3 ml of chloroform; after this, the lead and copper were transferred to the aqueous layer by shaking up with 2 lots of 2 ml of nitric acid; copper was extracred from the latter with dithizone.

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TABLE 1

Copper introduced in γ	Copper found in the precipitate in %	Copper found in the chloroform layer in %
80	98	--
40	95	--
30	97	--
20	67	99
10	34	100
5	24	105

Results of these tests are given in Table 1.

As can be seen from Table 1, with decreasing copper concentration, starting at 30 γ in 10 ml, the amount of it trapped in the precipitate decreases sharply. If the precipitate which forms after partial precipitation of the lead is extracted with chloroform, the copper goes over completely into the chloroform layer. This fact is in complete agreement with the thesis advanced by Babko [4]; according to Babko, during extraction of reaction products with a non-miscible solvent, equilibrium is displaced toward formation of the final product.

2. Concentration of Copper from Cadmium and Lead Salt Solutions by Means of Diethyldithiocarbamate

Diethyldithiocarbamate forms colorless or colored precipitates with a number of metals [5]; we were unable to find any data on the solubility of these precipitates in the literature. Accordingly, in choosing mixtures of metal salts which would be suitable for our purpose, we followed Kuznetsov's precepts [6], according to which a parallelism can be observed between reactions with organic and inorganic reagents possessing similar functional groups. In the case of diethyldithiocarbamate, it may be postulated that it forms with metals, compounds whose solubility in water changes in the same order as the sulfides. On the basis of these considerations, we choose cadmium and lead as macro-components. Copper was the micro-component, while the impurities consisted of metals which are normally present in cadmium and lead as contamination, and form colored compounds with diethyldithiocarbamate.

a) Determination of Copper in Cadmium Salts. Technical requirements specify determination of lead, zinc, iron, and copper in cadmium; of these, lead and zinc, like cadmium itself, form white precipitates with diethyldithiocarbamate. Thus, in developing a diethyldithiocarbamate method for determining copper in cadmium it was only necessary to determine the effect of iron; nevertheless, in a number of tests, we also added 2 mg each of lead and zinc, which, as was shown, did not affect copper determination.

The solution of cadmium chloride used for the tests, was freed from copper by extraction of the latter as the diethyldithiocarbamate with chloroform. Solutions of iron, lead, and zinc salts were purified by partial precipitation as sulfides.

Experiments on copper determination were carried out as follows: to the cadmium chloride solution was added solutions of copper, and iron, 1 ml 1 N nitric acid and 2 ml of 0.1% sodium diethyldithiocarbamate, after which copper was extracted with 2 lots of 2 ml chloroform. A standard was prepared by extracting copper from an aqueous solution acidified with nitric acid. Comparison of the colors were carried out in the chloroform layer in a visual colorimeter.

Results are given in Table 2.

On the basis of the results given in Table 2, it is possible to conclude that copper as the diethyldithiocarbamate can be quantitatively extracted from a solution of a cadmium salt, and that iron does not interfere with copper determination at iron contents of up to 0.05 mg.

b) Determination of Copper in Lead Salts. Of the metals which form colored precipitates with diethyldithiocarbamate, bismuth, iron, nickel, and cobalt, as well as copper, can be present as impurities in lead. Lead itself forms a white precipitate with this reagent.

Experiments were carried out in exactly the same way as for determination of copper in cadmium salts, using solutions of the metal salts (analytical grade) purified by partial precipitation with hydrogen sulfide. Results of these experiments showed that contamination by bismuth, iron, nickel, and cobalt in amounts permitted by All-Union Standards for Analytical Grade lead nitrate does not prevent determination of copper down to

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TABLE 2

Amount of 1 M Cadmium chloride taken in ml	Copper added in γ	Iron added in mg	Copper found in %
3	5	--	100
3	10	--	98
10	10	--	102
20	10	--	98
10	10	0.05	100
10	10	0.1	105
3	10	0.2	135

0.0001%. With increasing amount of impurities up to the limits shown in Table 3, bismuth and iron were observed to shift over into the chloroform layer, as a result, the results obtained were on the high side. Nevertheless, even in these cases, satisfactory results were obtained, under conditions where the standard was prepared by extracting copper from test solution, after extracting the copper to be determined from it, (see below).

c) Determination of Copper in Nickel and Cobalt Salts. Results of tests given in Table 3, led us to think that lead ions may act as a regulator of the concentration of free diethyldithiocarbamate during extraction of copper from nickel (cobalt) salts also. Nevertheless, tests showed that on increasing the amounts of nickel and cobalt to more than 0.1 mg in 10 ml of lead nitrate solution, they start to be extracted in appreciable amounts by the chloroform and impart a color to the latter. In addition, even for an amount of nickel of 1 g, only ~83% of the copper goes over into the chloroform layer**.

TABLE 3

Amount of 1 M Lead Nitrate taken in ml	Copper added in γ	Amount of impurities added in mg	Copper found in %	Amount of 1 M Lead Nitrate taken in ml	Copper added in γ	Amount of impurities added in mg	Copper found in %
20	10	--	99	10	10	0.1 Fe	100
20	5	--	100	10	10	0.5 Fe	105
10	10	0.10 Bi	100	10	10	0.1 Ni, Co. Fe & 0.01 Bi	100
10	10	0.25 Bi	115				
10	10	1.0 Ni	96	10	10	0.1 Ni, Co. Fe & 0.05 Bi	115
10	10	1.0 Co	100				

Complications connected with the transfer of some of the nickel (cobalt) into the chloroform layer, and the incomplete extraction of copper, where overcome as follows: errors were compensated for, by preparing a standard by extracting a known amount of copper from test solution after extracting the copper to be determined from it. Under these conditions, both nickel (cobalt) and copper were distributed between the solvents in equal proportions. As a result, the color of the chloroform extract of test solution and that of the standard solution will be weakened to an equal extent, because of incomplete extraction of copper, while they will be strengthened to an equal extent because of extraction of some of the nickel (cobalt).

Copper was determined in nickel (cobalt) nitrate as follows: to 10 ml of 1 M lead nitrate was added a known amount of copper and nickel (cobalt) solutions, followed by 1 ml of 1 N nitric acid an an exactly measured volume (4 ml) of 0.1% sodium diethyldithiocarbamate solution, after which copper was extracted with two lots of 2 mls of chloroform. A standard was prepared by adding copper to the aqueous solution left after removal of the copper to be determined, followed by addition of 2 ml of diethyldithiocarbamate solution; subsequent procedure was the same as for the first extraction***. Comparison of the colors of the chloroform solutions, as in previous

* We did not try to determine smaller amounts of copper.
** We determined the amount of copper extracted by the chloroform by comparing the color of the chloroform solution obtained by extracting copper from 10 ml of 1 M lead nitrate and 1 g of nickel, with the color of the united extracts, copper -- from an aqueous solution, and nickel -- from a solution of lead nitrate.
*** For amounts of nickel (cobalt) greater than 0.3-0.4 g, some products of a yellow-brown color were extracted by the chloroform, the colors produced by these compounds disappeared after 10-15 minutes.

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TABLE 4

Amount of nickel (cobalt) taken in g	Copper added in γ	Co, per found in %
0.05 Ni	10	100
0.1 Ni	10	95
0.2 Ni	10	97
1.0 Ni	10	100
0.025 Co	10	100
0.1 Co	10	97
1.0 Co	10	96

instances, were carried out in a visual colorimeter, it would be better however, in the given instance, to carry out colorimetric measurements in a photocolorimeter.

Results on the determination of copper in nickel and cobalt salts by the method suggested, as can be seen from Table 4, are completely satisfactory. One whould bear in mind however, that the change in color with change in copper concentration does not strictly follow Beer's law, since a constant light absorption determined by nickel (cobalt) is superimposed on the light absorption of copper diethyldithiocarbamate. Moreover, on the same principle, accuracy of colorimetric determination will also decrease with decreasing copper amounts in the test sample (according to our observations, satisfactory results can still be obtained for 10 γ copper in the test).

SUMMARY

1. Using concentration of copper from a solution of a lead salt by partial precipitation of the latter as an example, it has been shown, using 8-hydroxyquinoline as reagent, that copper is quantitatively trapped in the precipitate only when its concentration reaches a certain limit. With a decrease in copper concentration below this limit, the extent to which it is trapped in the precipitate decreases rapidly.

Quantitative removal of copper from the solution of a lead salt in this last instance, may be achieved by extracting the precipitate with a non-miscible solvent.

2. It has been shown that chloroform extraction of traces of copper as diethyldithiocarbamate from aqueous lead nitrate solutions, prevents extraction of bismuth, iron, nickel, and cobalt present as impurities, but does not prevent quantitative separation of copper. Cadmium chloride behaves similarly during extraction of copper from a solution containing iron as impurity.

On the basis of this action of the salts of lead and cadmium, methods have been developed for determining traces of copper in salts of lead, cadmium, nickel, and cobalt.

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THE PRECIPITABILITY OF STRONTIUM OXALATE IN THE

PRESENCE OF OTHER IONS

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In order to precipitate strontium completely as the oxalate, it is recommended that this salt be precipitated from an aqueous-alcohol solution using a definite excess of the precipitant — oxalic acid or ammonium oxalate [1, 2]. Since the solubility of strontium oxalate is relatively high in water—$2.3 \cdot 10^{-4}$ mol/liter [3], it is recommended also that the precipitate be washed with a saturated solution of strontium oxalate in order to cut down losses [4]. The presence in solution of salts which have a common ion with the precipitate, usually, increases its solubility and thereby decreases the amount precipitated. According to Pochinok's results [5], the solubility of strontium oxalate in 0.025 N ammonium chloride is 0.0957 g/liter, or $5.5 \cdot 10^{-4}$ mol/liter, while in 0.033 N ammonium chloride the corresponding figures are 0.1052 g/liter or $6.0 \cdot 10^{-4}$ mol/liter, i.e., 2.4-2.6 times its solubility in pure water.

In the present article we present results of experiments carried out to establish the effect of the presence in aqueous solution of potassium nitrate, potassium chloride, and ammonium acetate in various amounts on the precipitability and solubility of strontium oxalate, when equivalent amounts of strontium nitrate and ammonium oxalate are used and also when excess of the latter is used.

1. The Precipitability of Strontium Oxalate on Pouring Together Equivalent Amounts of Strontium Nitrate and Ammonium Oxalate

To 50 ml of a 0.01 N solution of ammonium oxalate was added a known amount of dry potassium nitrate, potassium chloride, or ammonium acetate; the solution was heated to the boil and 25 ml of a 0.02 N solution of strontium nitrate added to it. The concentration of the mixed salts at the moment when they were poured together was 0.0033 mol/liter. After 2 days the precipitate of strontium oxalate was filtered off, washed with cold water (~ 25 ml), dissolved in sulfuric acid and titrimetrically determined with 0.01 N potassium permanganate. Precipitability in the control test (in the absence of other salts) was taken as 100%. The solubility of strontium oxalate in mol/liter was calculated by means of the formula

$$\frac{(V_1 - V_2) \cdot K_1 \cdot K_2 \cdot 10^{-3}}{2} + 2.3 \cdot 10^{-4},$$

where V_1 is the volume of $KMnO_4$ in mls used in the control test; V_2 is the volume of $KMnO_4$ in mls used for test solution; K_1 is the normality coefficient of the $KMnO_4$; K_2 the coefficient for converting the volume of filtrate to 1 liter.

The difference $(V_1 - V_2)$ in mls of $KMnO_4$ corresponds to the difference in weight of the strontium oxalate precipitates which separate out from a solution which does not contain a salt with other ions (VI) and from a solution which contains such a salt (V_2), i.e. it corresponds to the amount of SrC_2O_4 which remains unprecipitated, as a result of the action of the salt with other ions. By multiplying this difference by the normality of the $KMnO_4$ (K_1), we get the number of milligram equivalents, while by dividing by two we get the number of millimols of

strontium oxalate, remaining under the influence of other salt in solution, the volume of which is composed of the volumes of strontium nitrate and ammonium oxalate poured together and the volume of wash water. This volume amounted to 100 ml (75 ml of solutions poured together + 25 ml of wash water) for the tests whose results are given in Tables 1 and 2. The coefficient (K_2) for converting to a volume of 1 liter is 10. The factor 10^{-5} is

TABLE 1

Precipitability of Strontium Oxalate in the Presence of KNO_3, KCl, and CH_3COONH_4 When Equivalent Amounts of $Sr(NO_3)_2$ and $(NH_4)_2C_2O_4$ (0.0033 mol/liter) are Used

KNO_3, KCl CH_3COONH_4 in mol/liter	Precipitability in %			Solubility in mol/liter		
	KNO_3	KCl	CH_3COONH_4	KNO_3	KCl	CH_3COONH_4
0.0	100.0	100.0	100.0	$2,3 \cdot 10^{-4}$	$2,3 \cdot 10^{-4}$	$2,3 \cdot 10^{-4}$
0.1	84.0	88.7	90.0	$5,6 \cdot 10^{-4}$	$4,4 \cdot 10^{-4}$	$4,3 \cdot 10^{-4}$
0.2	78.7	80.6	75.6	$5,9 \cdot 10^{-4}$	$5,9 \cdot 10^{-4}$	$7,1 \cdot 10^{-4}$
0.4	68.1	67.2	60.0	$8,3 \cdot 10^{-4}$	$8,3 \cdot 10^{-4}$	$10,2 \cdot 10^{-4}$
0.6	59.4	54.6	40.7	$11,1 \cdot 10^{-4}$	$10,6 \cdot 10^{-4}$	$14,0 \cdot 10^{-4}$
0.8	50.0	—	19.5	$13,2 \cdot 10^{-4}$		$18,1 \cdot 10^{-4}$
1.0	42.2	45.2	7.8	$14,8 \cdot 10^{-4}$	$12,3 \cdot 10^{-4}$	$20,4 \cdot 10^{-4}$

TABLE 2

Precipitability of Strontium Oxalate in the Presence of KCl, $NaCl$, and Excess $(NH_4)_2C_2O_4$

KCl, $NaCl$ in mol/liter	Excess $(NH_4)_2$ C_2O_4 in %	Precipitability in %		Solubility in mol/liter	
		KCl	$NaCl$	KCl	$NaCl$
0,6	—	100.0	100.0	$2,3 \cdot 10^{-4}$	$2,3 \cdot 10^{-4}$
0,6	25	52,5	50.4	$13.0 \cdot 10^{-4}$	$13,1 \cdot 10^{-4}$
0,6	50		64.0		$10,2 \cdot 10^{-4}$
0,6	100	85.6	75.9	$5,5 \cdot 10^{-4}$	$7,6 \cdot 10^{-4}$
0,6	100	86.4	89.0	$5,3 \cdot 10^{-4}$	$4,7 \cdot 10^{-4}$
0,6	200	89.0	140.0	$4,8 \cdot 10^{-4}$	

introduced in order to convert millimols into mols/liter. The solubility of strontium oxalate in pure water ($2.3 \cdot 10^{-4}$), is added to the value found for the number of mols of strontium oxalate which go into solution under the influence of the other salts present in solution.

Results are given in Table 1.

The precipitability of strontium oxalate in solutions containing potassium nitrate, is somewhat lower than in solutions containing potassium chloride (for equal molar concentrations). For a 1 M concentration of potassium nitrate, precipitability amounted to 42.2%, while for the same concentration for potassium chloride the value was 45.2%. The solubility of strontium oxalate increases 6.4 times in a molar solution of potassium nitrate, and 5.4 times in a molar solution of potassium chloride.

Ammonium acetate depressed the precipitability of strontium oxalate to a significantly greater extent than potassium chloride or nitrate; this can be explained by the fact that, under the precipitation conditions, ammonium acetate hydrolyzes strongly and the ammonia formed during the hydrolysis volatilizes leaving acetic acid, which has a dissolving action on strontium oxalate, to accumulate. In a 1 M solution of ammonium acetate, the precipitability of strontium oxalate falls to 7.8%, while its solubility increases 9 times.

2. Precipitability of Strontium Oxalate in the Presence of Potassium Chloride and Sodium Chloride when Excess Ammonium Oxalate is used.

To 50 ml of a 0.01 N solution of ammonium oxalate was added a certain excess of this salt, a known amount of potassium or sodium chloride, and the whole heated to the boil; 25 ml of 0.02 N strontium nitrate was then added. The strontium oxalate precipitate was then determined as usual with permanganate after 2 days. Results are given in Table 2.

The percentage of precipitability of SrC_2O_4 in 0.6 M potassium chloride and sodium chloride, when excess ammonium oxalate is used, increases but even when a 100% excess is used, precipitability still only amounts to 86-89%. For a 200% excess of ammonium oxalate in 0.6 M sodium chloride, a coarse heavy crystalline precipitate formed, the composition of this precipitate, as determined by the volume of $KMnO_4$ required, corresponds to the double salt $(NH_4)_2C_2O_4 \cdot 2.5\ SrC_2O_4$.

TABLE 3

Solubility of Strontium Oxalate in Aqueous Solutions of Potassium Nitrate

KNO_3 in mol/liter	H_2O in ml	Solubility of SrC_2O_4 in mol/liter
—	75	$2,86 \cdot 10^{-4}$
0.2	75	$7,76 \cdot 10^{-4}$
0.6	75	$12,85 \cdot 10^{-4}$
1.0	75	$16,00 \cdot 10^{-4}$

3. Solubility of Strontium Oxalate in Aqueous Solutions of Potassium Nitrate

Aliquots of 0.0484 g of $SrC_2O_4 \cdot H_2O$ were placed in beakers containing various weighed amounts of potassium nitrate, 75 ml of water was added, and the mixture left for 7 days with periodic shaking. After 7 days the undissolved strontium oxalate was filtered off, washed and quantitatively estimated with $KMnO_4$ as usual. In parallel, the number of mls of $KMnO_4$ required to oxidize 0.0484 g of $SrC_2O_4 \cdot H_2O$ was determined. Results are given in Table 3.

The solubility of strontium oxalate in distilled water, according to our results ($2.86 \cdot 10^{-4}$ mol/liter), proved to be higher than that given in the literature ($2.3 \cdot 10^{-4}$). It seems possible that the solubility of SrC_2O_4 in water has not yet been exactly determined; e.g., in Kentman's textbook [6], the solubility is stated to be 6.6 g/100 g water, which is equivalent to $660 \cdot 10^{-4}$ g/1000 g water, or $\sim 3.7 \cdot 10^{-4}$ mol/liter.

Results on the solubility of strontium oxalate in potassium nitrate solutions are fairly near the values obtained in experiments on precipitability (Table 1). The solubility of SrC_2O_4 increased 5.6 times in 1 M potassium nitrate. Changes in the solubility of strontium oxalate with concentration of potassium nitrate and potassium chloride are shown in the diagram given above.

Change in solubility of SrC_2O_4 with salt concentration: 1) KNO_3; II) KNO_3 (by precipitation); III) KCl (by precipitation).

SUMMARY

1. The percentage precipitability of strontium oxalate in aqueous solutions containing various concentrations of potassium nitrate, potassium chloride, and ammonium acetate has been determined; the solubility of strontium oxalate in these solutions has been calculated.

2. The effect of excess oxalate ions on the precipitability of SrC_2O_4 from aqueous solutions of potassium chloride and sodium chloride has been studied.

3. The solubility of strontium oxalate in aqueous solutions of potassium nitrate has been determined.

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SYSTEMATIC AND RANDOM ERRORS IN CHEMICAL ANALYSIS

V. V. Nalimov

The aim of any accurate measurement, including chemical analysis, is not only to get analytical results, but, in addition, to evaluate the reproducibility and correctness of the results obtained. This question has become very pressing at the moment when All-Union State Standards are to be drawn up for spectrographic methods of analysis. When specification tests are being carried out by various methods which differ in principle, it is unavoidable that conflicting results will sometimes be obtained; these conflicts can only be resolved correctly, when reliability limits have been established for each method, in this first instance, of course, for a chemical method. Methods of evaluating errors of reproducibility of chemical analysis are not particularly difficult — in recent years, both abroad, and in Soviet literature [1-4], many papers have appeared which recommend the widespread use of mathematical statistics for this purpose. Evaluation of systematic errors in chemical analysis is however considerably more complex. Usually, standard samples are used for this purpose in the laboratory. Nevertheless, no indications are given in the chemical literature, or in All-Union Standard Methods on chemical analysis, on how to evaluate and standardize systematic errors. In turn, this naturally leads to serious disagreements. Everyday experience shows that, in certain cases, analysis of the same test sample in different laboratories gives essential systematic deviations, despite the fact that, in both laboratories, it has been shown, by replicate analysis of the same standard, that systematic errors are absent. Shaevich [5], has shown that even in the case of analyses carried out with particular care, during preparation of standard samples of casts and steels, systematic deviations were observed between the results of different laboratories. Our work on a study of systematic errors in the chemical analysis of slags has shown that the magnitude of the relative systematic error depends essentially on the chemical composition of test material, and, accordingly, cannot be controlled by means of any one standard sample. There is plenty of evidence at the moment, which indicates that the use of one, or even of several standard samples, is not an effective method for calculating and standardizing systematic errors in chemical analysis. The reason for this is not clear enough. The aim of the present article is to try and clear up this question on the basis of the mathematical theory of errors.

We shall start off by giving a clear definition of the concepts of systematic and random errors. One can only talk about the random error of a chemical analysis when the number of measurements considered are clearly defined and limited. If a variable quantity belonging to this number of measurements, assumes a value which depends on chance, and a distribution function can be determined for it, then such a value can be called a random value [6]. Systematic errors — are errors which arise as a result of one or several definite causes, operating according to certain definite laws [7]. In order therefore to establish the presence of systematic errors, we must know what these laws are [8]; in this case, a systematic error can be regarded as a correction to be applied to the measurements. It is essential to emphasize that the difference between systematic and random errors is very relative — it depends on the number of measurements chosen for consideration, and this choice, by its very nature, is completely arbitrary. For example, if one considers a number of measurements of the diameter of some detail by means of a defective micrometer, then, in relation to this number of measurements, the error introduced by the defect in the micrometer, can be regarded as a systematic error. If then we consider a number of micrometers issued by the factory, the error in the manufacture of the micrometers can be regarded as a random error [9]. Let us take a second example, if we consider a number of measurements carried out at equal temperatures, then with respect to this number of measurements, the error will be a random one. If, then, measurements are carried out at strictly fixed temperatures, and the law is determined which defines how change in temperature affects the results of measurements, the temperature error can be regarded as a systematic one, and even as a correction to be applied to the measurement.

Chemical analysis is a complex measuring process, accordingly, it is necessary to approach the separation of errors into random and systematic errors with particular care. In studying errors of chemical analysis, it is necessary to examine the following numbers of measurements.

1. Let us assume that there is a statistic ensemble consisting of a number of measurements on one standard sample, carried out in one laboratory within a certain time limit. If we take the mean arithmetic value of the analytical results as the center of scatter, then henceforth we shall call the random error obtained with respect to this value, the reproducibility error. Usually, it is quite unjustified to assume that all the random errors of chemical analysis are confined to one reproducibility error. Further, if on carrying out a sufficiently large number of replicate experiments, there is discovered a persistent deviation between the mean value of the analysis and the specified results for the Standard Sample (SS), then we get a constant error, which is usually called the "systematic error" of the chemical analysis, and, it is assumed that it characterizes the systematic error of a chemical analysis as a whole, or at least for test materials, approximating in composition to that of the SS, though the reasons which give rise to this error, and the laws according to which this value which is constant usually remain unknown. Accordingly, on the basis of the definition given above, only errors of reproducibility can normally be the object of the application of mathematical statistics in chemical analysis, since by its very nature, mathematical statistics which is based on the theory of probability, can only deal with random errors. Existing All-Union Standards for chemical analysis also only confine themselves to requirements following from errors of reproducibility, — this follows from the work of Shaevich [5], and also from our own work on the study of errors of reproducibility during analysis of carbon steels*. Thus the large group of errors which have been united without justification under the one term "systematic error", usually remain outside the scope of investigation of the research worker**.

2. Let us assume that this same SS be continued to be analyzed in the same laboratory over more or less long time intervals. Now, that value which was formerly constant with respect to the previous number of measurements, becomes a variable quantity. This arises as a result of the fact that a number of factors assumed to be constant during the time the original measurements were made, may later become variables. With time, the purity of the water and the reagents change; the weights suffer from wear; pressure changes, as do humidity, temperature, illumination of the place of work, etc. All these factors, to some extent, will affect the analytical results.

3. Let us also assume that the SS is analyzed in different laboratories — we shall then get a new set of

Fig. 1. Histograms for the results of analysis of two silicates according to Fairbairn [10].

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* It is shown in this article, that the assumption made in GOST 2331-43 (All-Union Standard), during analysis of steels for C, S, and P, can be represented by an equation: GOST assumes $\frac{2\sigma_{reproducibility}}{\sqrt{n}}$, where $\sigma_{reproducibility}$ is the square of the reproducibility error; n is the number of replicates on which analysis is based; for carbon n = 4; and for sulfur and phosphorus n = 2.

** In the overall balance of the errors of a chemical analysis, the reproducibility error plays a small part; accordingly, some authors [14], agree that mathematical statistics should not be used for exposing the actual errors of a chemical analysis.

measurements, which differs essentially from the first set — here again, a magnitude which was constant in the first instance has become a variable. At the same time, the statistical ensemble, consisting of a number of measurements of one test object in different laboratories, may differ essentially from the statistical ensemble, obtained from a number of analyses of another test material in the same laboratories. The variation coefficient (relative square error) obtained for one of these ensembles, does not permit one to forecast what the analogous value for another ensemble will be; the laws of distribution of these ensembles can also vary. This is illustrated by the histograms borrowed from the literature [10], for the results of the analysis of two silicate samples of granite and diabase for their CaO and MgO content, which was carried out in 24 laboratories in various countries.

4. Finally, let us consider the statistical ensemble, consisting of a number of measurements of standards differing in composition (of one type) carried out in one laboratory in the course of a short time interval. We shall take the certified results (i.e. the ones given with the samples) as being the center of scatter — we shall calculate the error for each sample as a difference between the certified results and the mean values of the analytical results, and we shall express the errors in terms of relative percentages. This rather unusual statistical ensemble we shall consider in greater detail — it is of particular interest, since, if in the course of practical work, for the control of the correctness of an analysis, one should take only one SS as well as the unknown samples to be analyzed, then these samples together with the standard sample can be regarded as a selection from the statistical ensemble defined above.

In the study of the relative errors of test samples which differ in composition, some of the active factors which act in a constant fashion become variables, since the magnitude of the relative errors, introduced by the constant factors, depends, in a number of cases on the concentration of the test component. E. g. during gravimetric analysis, impurities in the precipitate as the result of insufficient purity of water, or reagents, contamination by the containing vessel, etc. can give a relative error which depends on the concentration of the test component. Coprecipitation of elements which accompany the test element gives a relative error which depends on the concentration of both the test component, and on that of the accompanying elements. Titers and factors can also depend on the concentrations of accompanying elements in volumetric and photocolorimetric methods of analysis. Characteristics of the phase composition of test samples (on which the solubility of test samples depends) can, in certain instances, give a random error for the number of measurements of various test samples considered by us.

The following is of interest as an example: the frequently recurring instance of an error which depends on the concentration of test component. If there are several standards, then, in the case of volumetric and photo-colorimetric analysis, it is possible to construct graphs in which concentration is plotted along the abscissa, and the number of cm³ used for titration on the ordinate; then the cotangent of the angle slope of this line will be the titer, while the segment cut off along the ordinate will be the number of cm³ used for titrating — the "blank" (Fig. 2). Determination of the titer by means of several SS does not lead to doubt. Nevertheless, the analyst has usually only one SS at his disposal, and the number of cm³ used for the "blank" is used as the second point. Direct determination of the "blank" is bound up with a number of difficulties as a result of the weak color — the relative error in determining this point is very large. In addition, it must be borne in mind, that in the "blank", only the concentration of test component should be equal to zero, while the concentrations of the other components (base and accompanying elements) should remain unchanged — it is impossible to fulfil this requirement in practice during direct experimental determination of the "blank". Determination of the titer by means of an

Fig. 2. Graphical determination of the titer by means of several standard samples (complete line) and by means of a standard sample (dotted line).

unreliably determined "blank", is equivalent to exchanging the true curve, designated in Fig. 2, by a complete line, by an incorrect curve designated by the dotted line. Comparison of these two lines show that, in this case,

the magnitude of the error and its sign, depend on the position of the test sample relative to the standard, by means of which the titer is established. In instructions, it i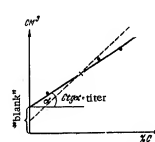s usually stated that a SS should only be used for establishing the titer, in the analysis of samples approximating in composition to the given SS; this leads to a decrease in the error, but, in principle, does not eliminate it*. We analyzed 40 samples of slag for their FeO_{total}, and calculations were made by two methods — by means of a graph constructed on the basis of several standards (combined SS's), and by means of a titer which was determined on the basis of one SS and a blank, — the deviation which was determined solely by this fact, gave a relative square error of 3.7%.

Thus, in a statistical ensemble, consisting of the analysis of a number of samples differing in composition, a new random error appears, which is transformed into a constant, if one is confined to a number consisting of the analysis of one test sample. Determination of this value is bound up with considerable difficulties. If we have a series of standards and carry out calculation of the errors with respect to the certified results, then we get the total error:

$$\sigma_{\Sigma} = \sqrt{\frac{\sigma^2_{reprod.}}{n} + \sigma^2_{random\ chem.} + a^2}, \qquad (1)$$

here $\sigma_{reproducibility}$ is the reproducibility error for one analysis, n is the number of replicate tests, on the basis of which the analysis is carried out; $\sigma_{random\ chem.}$ is the random error, determined by the characteristics of the chemical and phase composition of the test samples; a is a constant error** (displacement of the actual scatter center of the random errors with respect to the specified results, on the basis of which the errors are calculated).

If we have a series of test samples which differ in composition, and which have been analyzed by methods which differ in principle in one, or several laboratories, then the deviation in the analytical results will be represented by the following error:

$$\sigma_{\Sigma\ I-II} = \sqrt{\frac{\sigma^2_{reprod.\ I}}{n_I} + \frac{\sigma^2_{reprod.\ II}}{n_{II}} + \sigma^2_{random\ chem.\ I} + \sigma^2_{random\ chem.\ II} + (a_I - a_{II})^2}, \qquad (2)$$

here the indices I and II denote the errors of two different methods; the values a_I and a_{II} are calculated algebraically. Finally, if a series of samples are analyzed in two different laboratories by the same method, or by methods which only differ in details, then the analytical results of the two laboratories can, generally speaking, be correlated between each other, when

$$\sigma_{\Sigma\ I-II} =$$

$$= \sqrt{\frac{\sigma^2_{reprod.\ I}}{n_I} + \frac{\sigma^2_{reprod.\ II}}{n_{II}} + \sigma^2_{random\ chem.\ I} + \sigma^2_{random\ chem.\ II} - 2r\sigma_{random\ chem.\ I}\sigma_{random\ chem.\ II} + (a_I - a_{II})^2}, \qquad (3)$$

here r is the correlation coefficient between the analytical results of the two laboratories. In this case, $\sigma_{\epsilon I-II}$ is a very indeterminate quantity; here we have an equation with many unknowns, and, at the same time, the correlation coefficient is not known to us. In a special, limiting case, the work of the two laboratories may be in such good agreement, that we can have $r = \sim 1.0$; $\sigma_{random\ chem.\ I}$ is approximately equal to $\sigma_{random\ chem.\ II}$, a_I approximately equal to a_{II}. In this case, $\sigma_{\epsilon I-II}$ will be determined only by the reproducibility errors. Thus, if during interlaboratory control, when the same type of method is used, a small value is obtained for $\sigma_{\epsilon I-II}$, this still does not testify to the real absence of errors. During particularly careful chemical

* The use of SS for establishing the titer, from a formal point of view, can be regarded as an unjustified introduction of the same correction to test samples differing in their composition.
** The use of dispersion analysis can be recommended for individual calculation of errors entering (1), and for the determination of their significance. We intend to devote a separate article to this question.

analysis, e.g. the preparation of standards, very often, intensive and expensive efforts are directed at achieving good agreement for the results of chemical analysis in different laboratories, when it is quite possible, that in a number of cases, these efforts are really only directed at getting the correlation coefficient to approach unity, and not to an actual attempt at cutting down the errors.

It is exceedingly important that we clear up the law of the distribution of this new random magnitude. We shall consider this question primarily on theoretical grounds. According to the central limiting theorem of Lyapunov, total θ of independent random magnitudes $x_1, x_2, \ldots x_\nu$ for a sufficiently large ν, has a normal distribution. even when the independent random magnitudes $x_1, x_2 \ldots$ have an arbitrary distribution under the condition that all random magnitudes considered are of approximately the same order, i.e. there should not be such random values among the magnitudes $x_1, x_2, \ldots x_\nu$, as are greater than most of the other magnitudes. In the special case, where the unknown variables are distributed normally, the sum will be distributed normally for any ν. In the case we are considering viz., a number of measurements of samples differing with respect to their composition, we have to deal with a large number of independent variables (their number, is, of course, greater than we enumerated above); the laws of distribution of these variables, are, generally speaking not known to us, but, we can at least assume that when methods which have been worked out well are used, and the laboratories in which the work is carried out are properly organized, the dominating factors should be absent — this permits one to assume that the random error, whose scattering is characterized by $\sigma_{random\ chem.}$, should obey Gauss' law. The normal law immediately breaks down, if one of the components, even the test component, varies within very wide limits, and is converted in this way into a dominating factor. E. g., there is hardly any sense in uniting in one statistical ensemble, test samples in which the test component varies within limits ranging from some hundredths of a percent to 1-10% but, if for some reason, such unification is carried out, we get a correlation link between the value of σ and the concentration of the test component, as shown in Shaevich's work [5]. Thus, the random error which is characterized by the characteristics of the chemical composition of the test samples, will have a normal distribution only when certain conditions are fulfilled; for reproducibility errors, these conditions are almost always fulfilled automatically, and consequently, for reproducibility errors, there is practically always a normal distribution.

When considering the distribution of analytical results for samples differing in composition, it is always necessary to take into account the presence of a constant factor, which shifts all the deviations to one side, as a result of which one gets an asymmetric distribution of signs. Only the absolute magnitude of the errors and their distribution are of essential significance in analytical work. If we confine ourselves to the consideration of absolute magnitudes only*, then we get the following distribution function:

$$\varphi(x) = \frac{1}{\sqrt{2\pi} \cdot \sigma_0}\left[e^{-\frac{(x-a)^2}{2\sigma_0^2}} + e^{-\frac{(x+a)^2}{2\sigma_0^2}}\right], \qquad (4)$$

here σ_0 is the mean square deviation of the original normal distribution; a is the shift in the center of this distribution. In the case where $a/\sigma_0 < 1.0$, distribution (4) can be replaced by the function:

$$\varphi(x) = \frac{2}{\sqrt{2\pi} \cdot \sigma_0}e^{-\frac{x^2}{2\sigma_0^2}} \qquad (5)$$

this is a Gauss distribution on the basis of the descending side with doubled ordinates. Function (5) can, to a first

* One often comes up against consideration of the absolute values of the deviation in machine construction, during a study of the quality and accuracy of production — this question is treated in detail by Borodachev [11].

approximation, describe the statistical ensemble which we are considering, which consists of a number of samples differing in composition, i they are formed in such a way that a dominating factor is absent. Let us consider as an example the analysis of 50 slag samples for CaO, SiO_2, and total Fe, which was carried out in two different laboratories by two different methods. In Table 1 are given the results characterizing the distribution of errors for interlaboratory control of slags; here we have a clear-cut case of sign asymmetry. On changing over to absolute values of the errors, we get a distribution, which, as calculation of the criterion of agreement shows, is described fairly well by distribution function (5).

TABLE 1

Components determined	e_i $x-11$ in %	Number of errors with the same sign in %	Probability of a random deviation from distribution (5)	
			according to Pearson	according to Kolmogorov
CaO	6.05	93	0.13	0.79
SiO_2	8.5	98	0.08	0.33
Total Fe	5.7	24	0.44	0.39

Taking into account the normal distribution of errors determined by the characteristics of the chemical and phase composition of test samples, one can make a critical approach to the question of how it is possible to establish reliability limits for chemical analysis, if standard samples are used for this purpose. We shall start off with a schematic and rather abstract consideration of this problem; let us assume that we analyze $\underline{n}$ standards at the same time as the unknown test samples; at the same time, we assume that standards and test samples belong to one general set, the scatter of which is determined by $\sigma_{random\ chem.\ general}$. One can solve the problem of the upper possible limit for the value of $\sigma_{random\ chem.\ general}$, if $\bar{\sigma}_{random\ chem.}$ is known on the basis of analysis of standards and a comparison of these results with certified results ($\sigma_{reproducibility}$ is not taken into account, since it is assumed that each standard has been made from a large number of replicates). In this case:

$$\sigma_{random\ chem.\ general} = \frac{\sqrt{n-1}}{\sqrt{\chi^2}}\ \bar{\sigma}_{random\ chem.} \qquad (6)$$

the value of χ^2 is given by Pearson's distribution $P(\chi^2, n-1)$.

Further, if the center of displacement a (the mean relative deviation from certified results) is determined by means of $\underline{n}$-standards (standard samples), then it would be incorrect, during the analysis of some unknown test samples to expect a deviation from the true content within the limits of the magnitude of a. The maximum possible deviation of the relative error of analytical results from the center of the displacement a is determined by the equation:

$$(a-x_{an}) = t \cdot \sqrt{\frac{n+1}{n}}\ \bar{\sigma}_{random\ chem.} \qquad (7)$$

where $\underline{t}$ is given by Student's distribution $S(t, n-1)$. Equations (6) and (7) can be solved for any $n \geq 2$; having set a reliability of 0.95, we get the following solutions

$n = 2$; $\sigma_{random\ chem.\ general} = 16\bar{\sigma}_{random\ chem.}$; $(a-x_{an}) = 16\bar{\sigma}_{random\ chem.}$

$n = 3$; $\sigma_{random\ chem.\ general} = 4.4\bar{\sigma}_{random\ chem.}$; $(a-x_{an}) = 5.0\bar{\sigma}_{random\ chem.}$

$n = 4$; $\sigma_{random\ chem.\ general} = 2.9\bar{\sigma}_{random\ chem.}$; $(a-x_{an}) = 3.6\bar{\sigma}_{random\ chem.}$

. . . .

$n = 10$; $\sigma_{random\ chem.\ general} = 1.7\bar{\sigma}_{random\ chem.}$; $(a-x_{an}) = 2.4\bar{\sigma}_{random\ chem.}$

These calculations show that, even in this case, when standards and test samples can be regarded as a random choice from a set with normal distribution, for establishing reliability limits for a small number of standards, it is necessary to multiply $\bar{\sigma}$ random chem. by a very large coefficient. From this it becomes quite obvious why, sometimes, the analysis of some sample or other gives a result which is far from the true content of the test component, though the standards which were analyzed at the same time as the test sample gave sufficiently good agreement with the certified results. In particular, these calculations permit one to understand why such large errors can be obtained during inter-laboratory control of slag (Table 1), though both laboratories check the correctness of their work on one and the same standards.

In practical work, application of formulas (6) and (7) for establishing confidence limits is connected with certain difficulties*, since in such cases the following conditions must be fulfilled: standards and test samples must be a random choice from a set, in which there is no very marked deviation from a normal distribution. The latter condition is deliberately formulated rather loosely, since, it is known from published results [12], that experimental verification has demonstrated the possibility of using Student's distribution, on which formula (7) is based, even when deviation from a normal distribution is observed in the general set. If test samples and standards (with respect to the test component) lie within the concentration range, the limits of which do not differ by more than a factor of 2, then there is no foundation for fearing a large deviation from normal distribution. Test sample and standards can be regarded as random choices from one and the same set, consisting of samples differing with respect to composition, if the standards differ essentially from one another in their chemical composition. In order to verify the possibility of using equation (7) under the restrictions indicated, we prepared in our laboratory 10 synthetic slag standards which differed in their chemical composition; each of these standards was then subjected to replicate analysis using the same simplified methods as were used for a series of tests. The standards were divided into groups in which the test component content was changed within the limits 1:2 for each group; by means of equation (7) the ratio of the maximum expected error to the actually determined maximum deviation from the certified results was calculated. Results of these calculations are given in Table 2. Here, in the first short line are given results obtained for calculations for $n = 3$; at the same time three standards were deliberately chosen such that they had a minimum deviation from the certified results.

TABLE 2

	CaO	SiO_4 wt.	SiO_4 ϕ/ K	$Fe_{tot.}$	Mg	MnO	Al_2O_4
Concentration range	22–47%	12–25%	25–38%	12–25%	25–38%	3–7%	3–6%	2–4%	8–10%	1–2%	3–7%
Ratio found error to calc. error [by eq. (7); $n = 3$, $a = 0.95$].	0:7	2:1	3:9	1:5	1:3	2:0	1:3	1:7	1:2	3:1	0:8
Ditto for $n = 4–9$	0:8 $n = 9$	1:4 $n = 5$	—	2:0 $n = 5$	—	1:7 $n = 6$	2:1 $n = 4$	1:0 $n = 4$	—	0:8 $n = 5$

* Formula (7) is usually used for solving the problem of whether the $(n + 1)$ determination is compatible with the other $\underline{n}$ measurements. Here, it is necessary to solve the opposite problem: to lay down conditions under which analysis of $\underline{n}$ standards will be compatible with the analysis of the $(n + 1)$ test sample, and then, on the basis of equation (7) establish confidence limits for analysis of test sample.

The results in Table 2 show that, under certain conditions, equation (7), for $n \geq 3$, can be used for establishing reliability limits. Formally, equation (7) can also be used for $n = 2*$; nevertheless, establishment of reliability limits for $n = 2$, is hardly worthwhile in practice, since, in such cases, on account of the small number of standards, one would have to use a very large coefficient, and this, in many cases, will inevitably lead to very high values for the reliability limits.

Reviewing the position, one can indicate the following methods of evaluating errors, determined by the characteristics of the chemical and phase composition of test samples.

1. The Use of Standards. Reliability limits can be established by means of formulas (6) and (7), when the following conditions are fulfilled: a) number of standards $n \geq 3$; b) test samples and standards are chosen so that the test component lies within a concentration range, the extreme points of which are in the ratio of $1:2$; c) the standards should differ essentially from each other with respect to their chemical composition (in, some cases their phase composition as well). Despite all limitations, this method is not free from a number of arbitrary assumptions and its application in each specific case requires a careful analysis of all available material.

2. Checking the Same Sample by Methods which Differ in Principle. In such cases one comes up against the following difficulties: a) even in the case of methods which differ in principle, analytical results may be related to each other in a correlative way; this no doubt happens, if, during development of one method, one takes as a basis the results of another, i.e. to consciously produce agreement between the two methods**. This is confirmed by the fact that sometimes the results of analysis of samples carried out within one laboratory by methods which differ in principle, differ less among themselves than the analyses of the same samples carried out in different laboratories but by the same method; b) if, even by some indirect methods it has been established that correlation is absent in the results of an analysis carried out by two different methods, equation (2) cannot be solved, since there are several unknowns; it must be replaced by the equations:

$$\sigma_{\Sigma\,I-II} = \sqrt{\sigma_{\Sigma I}^2 + \sigma_{\Sigma II}^2}; \quad \sigma_{EI} = \sigma_{EII}; \tag{8}$$

it is only by means of this method, which is essentially a completely arbitrary method, that it would be possible to have a rough evaluation of the error we are interested in for each method taken separately.

3. Analysis of test samples, carried out in different laboratories by the same method, or by methods which differ very little from each other, can give a correct representation of the actual mistakes only in the case where the results of the laboratory do not agree among themselves, i.e. if the correlation coefficient in equation (3) is near to zero. In such a case, again, equation (3) must be quite arbitrarily substituted for by equation (8).

4. Finally, it is possible to study the reasons for the existence of errors determined by the characteristics of the chemical composition of test samples***. From a formal point of view this is equivalent to a change-over from random errors to systematic ones. If the errors of a chemical analysis were confined to reproducibility errors and systematic errors, the reason for the appearance of which is known and can be firmly established, the question of calculation of errors would be solved very readily.

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* For $n = 1$, the mathematical scheme considered is not applicable. In this case, the deviation between certified results and the mean analytical result for the standard cannot be resolved into a variable and a constant component.
** E.g. in order to get agreement between the results of spectrographic and chemical analysis, special precautions are often resorted to: choosing special excitation conditions, parallel displacements of graphs for samples differing in composition, breaking the graphs, etc. It is possible that in certain cases, perhaps rare, it may also be necessary merely to increase the value of the correlation coefficient in equation (3) to values approximating unity.
*** E. G. compilation of a complete material balance for gravimetric methods of analysis using spectrographic methods of study, of the method of tagged atoms, and other methods for studying composition of precipitates, filtrates, etc. (an example of such a study is given in [13], where the use of spectrographic methods for correcting gravimetric analysis is demonstrated).

Analysis of chemical errors, carried out in this paper, shows that all possible methods of evaluating the correctness of a chemical analysis, apart from the last one, are based on a number of arbitrary assumptions; accordingly, they must be considered as only rather rough orientating methods. As far as the last method is concerned — studying the reasons for the mistakes, — it is free from any arbitrary assumptions, but is characterized by being extremely cumbersome and accordingly can only be seldom used in practice.

SUMMARY

Chemical analysis is a complex measuring process, which differs in principle from elementary measuring processes which are dealt with in metrology. In chemical analysis, in addition to the random error of reproducibility, there is one further random error, which is determined by the characteristics of the chemical (and sometimes, phase) composition of test samples. The distribution law of this error is considered. Various methods of evaluating the magnitude of this error are critically considered; conditions under which standards can be used for establishing reliability limits are established.

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A MANOSTAT AND RECEIVER FOR VACUUM DISTILLATION IN COLUMNS

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Analytical distillation on columns is widely used during analysis of mixtures of organic materials in order to get accurate fractionation. In recent years such distillations have more and more often been carried out not only at atmospheric, but also at reduced pressures. For working under vacuum it is easy to use normal laboratory columns with packing of various types, e.g. of the type we described previously [1]. Nevertheless, in order to carry out successful analytical distillations, the columns should be provided with certain additional attachments: first of all with a manostat — an apparatus which ensures a constant pressure in the system during distillation —, and a receiver, by means of which it is possible, without interrupting distillation, to select an unlimited number of fractions.

Carrying out analytical distillations under a vacuum, without the aid of a manostat, requires practically undivided attention from the analyst if a constant pressure is to be maintained in the system; even then the results obtained are not so reliable as those that can be obtained when the pressure is automatically regulated. Actually, during vacuum distillation, comparatively small variations in the pressure have a relatively large effect on the temperature of the saturated vapor in equilibrium with liquid, and is considerably greater than at atmospheric pressure. As an example one can cite results for variation of the saturated vapor in equilibrium with the liquid, with the pressure, for the case of diethylphthalate, 1-ethylnaphthalene, and 1,7-dichlorooctamethyltetrasiloxane [2]. According to calculation, a change in pressure of 1 mm leads to a change in temperature of the vapor of 6° in a vacuum (at 3-4 mm) and to less than 0.1° at atmospheric pressure. Thus, a change in pressure during vacuum distillation leads to a change in the temperature of the saturated vapor, without changing its composition; it destroys the equilibrium established, and, consequently, affects trickling, reflux number, and other operational conditions in the column. Moreover, in various parts of the system the pressure does not change evenly, and as a result it may show up differently on the thermometer bulb and on the manometer; this leads to incorrect determination of the boiling temperature.

A number of manostats are described in the literature which can be used for use with laboratory columns [3]. In the present communication we described a manostat which is distinguished by its simplicity of construction; it is convenient to use, and gives good results in practice.

When analysis is carried out with the aid of rectification, usually a distillation curve is "taken", i. e., a curve is drawn on the basis of the volume of distillate registered and the vapor temperature; this permits one to get an idea of the qualitative and quantitative composition of the mixture distilled. When carrying out analytical distillation under vacuum, it is necessary to provide the column with a receiver which will enable many fractions to be selected without interrupting the readings necessary for constructing a distillation curve. A receiver of this type is described in the present article; this has already been used with success in our laboratory and is now being manufactured by one of our factories.

Manostat. The manostat is an all-glass one (Fig. 1). Mercury is used as the sealing liquid; it is poured into chambers A and B till on opening tap 3 it touches all the surface of the lower edge of the porous glass disc 1.

The principle of the operation of the manostat consists of the following: the requisite pressure is established in the system, after which the taps are closed (Fig. 1); a "standard" pressure will then be maintained in chamber A. If the pressure in the system, and consequently in chamber B, connected with the system isolated from the pump by

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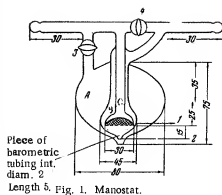
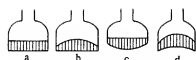Piece of barometric tubing int. diam. 2 Length 5. Fig. 1. Manostat.

Fig. 2. Test forms of the porous discs.

means of tap 4, exceeds the pressure in A, then the mercury will flow back from A into B, since they are connected to each other, like communicating vessels, through opening 2. As a result, the level of mercury in B drops a little and opens up the porous disc a little. Then, through the latter, air will be sucked from B, into C which is connected with the pump until a pressure equal to the standard pressure in A will be established in B, and consequently through all the system. When this occurs, the level of the mercury in A and B will become equal and the mercury again closes the porous disc, cutting off, thereby, the exit of the air from the system into C.

During actual operation, all of this is realized as follows. The manostat is fitted into the system between manometer and vacuum pump. The system is evacuated on opening the manostat taps. When the manometer indicates the requisite pressure, both manostat taps are immediately closed. Under these conditions, for normal operation of the manostat, it is necessary to have a pressure drop of not less than a certain definite pressure value (see below) between the vacuum pump and the system in which constant pressure is being maintained.

If the amount of mercury in the manostat corresponds exactly to the level indicated above, the manostat will, in the course of many hours, maintain a constant pressure in the system without further attention from the operator. If the amount of mercury is greater or less than the amount indicated, then the pressure finally established in the system will differ from the pressure at which the taps are closed to a greater or lesser extent.

When the operation is finished, it is first of all essential to open both manostat taps immediately; air can then be let in. In fixing the manostat, it is necessary to make sure that its porous disc is arranged as horizontal as possible, even visually, and also that the manostat is protected from appreciable temperature changes in the surrounding medium.

As tests we carried out showed, operation of the manostat depends on the shape of the porous disc and on its porosity. Results of tests on discs of different porosity showed that a porous disc from a No. 1 filter is not suitable for a manostat, since the mercury filters through it even for a pressure difference on opposite sides of only 30 mm Hg. Mercury only starts to filter through a No. 2 filter at a pressure difference greater than 150 mm. Discs made from No. 3 and 4 filters permit work at any residual pressure right up to 760 mm; nevertheless, the rate of suction of air through a filter No. 3, and even more so through a No. 4 is considerably less than through a No. 2 filter. As a result of this, a manostat fitted with a disc made from a No. 2 filter best maintains a constant pressure in the event of an accidental or necessary letting of air into the system. Moreover, the minimum necessary pressure drop between pump and the system amounts to only 4-5 mm when a No. 2 disc is used, while it is not appreciably greater in the case of a No. 3 or a No. 4.

Thus, for regulating the pressure below 150 mm (and this is more often the case than not) a porous plate made from a No. 2 filter is best suited. When this is done, it cannot be assumed that the pressure difference between B and C exceeds 150 mm, i.e. one should not close the manostat taps until the pressure in the system has dropped below 150 mm, in order to avoid filtration of the mercury into C. If it is necessary to distill at pressures higher than 150 mm, one should use a manostat fitted with a porous disc made from a No. 3 filter. If however, only a manostat fitted with a No. 2 disc is available, one can still use such a manostat, as long as one ensures that air is let into a line connecting manostat with pump. This bleeding, which can be achieved by means of a T-piece fitted with a tap or clamp, is used for lowering (down to 150 mm or even less) the pressure difference between B and C.
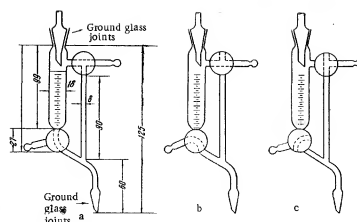
Fig. 3. Receivers: a) In the operating position; b) position of taps while switching cylinders; c) position of taps while evacuating the cylinder.

The shape of the disc, as was shown above, also affects the work of the manostat. Of the four types of porous glass discs tested, best results were given by the plano-convex disc (Fig. 2b). The use of such a disc cuts down the time required to establish a constant pressure, and increases the sensitivity of the manostat to changes in pressure in the system when air is let in. Discs of the shape indicated can be prepared when constructing a manostat by machining a lump of porous glass filter 5-7 mm thick. On fusing the disc in the apparatus, it should be tested for the minimum pressure at which filtration of mercury through the pores starts.

Receiver. The receiver is also an all-glass one. (Fig. 3). The bottom tap of the receiver is crescent shaped while the upper tap is a three way one. The ground glass joint to which the calibrated cylinder is connected, should be a normal one, or several cylinders can be fitted to one joint. The cylinders should be calibrated in 0.2 or 0.1 ml. Such calibrations of 0.2 or 0.1 ml should also be provided on the upper part of the receiver to 2/3 of its height.

For establishing the requisite vacuum in the column and for taking distillate samples, the position of the taps should be that shown in Fig. 3a. For switching cylinders, the taps should be rotated into the position shown in Fig. 3b. In doing this, it is necessary first of all to turn the upper tap, and only after this has been done is the lower one turned. As a result, the pressure in the cylinder will become equal to atmospheric, after which the cylinder can easily be removed and replaced by another. The lower tap is then turned to the position shown in Fig. 3c, after which the upper tap is also carefully turned into the respective position, taking care, by observing the manometer, that the pressure does not change too rapidly. When the pressure in cylinder and system have returned to their former value, the upper tap is turned into the position corresponding to that shown in Fig. 3a, and the bottom tap then turned to its corresponding position. Since the air in the lower tap is still at atmospheric pressure, the tap must be turned very carefully.

Since the top part of the receiver is calibrated, taking of distillates need not be stopped during change-over of cylinders; accordingly, this operation does not interfere with getting the requisite results for constructing a distillation curve within the coordinates, distillate volume — temperature, which is usually necessary for evaluating the quantitative composition of the mixture being distilled.

If the manostats are imperfectly made (poor fit of tap 4, poor finishing of the lower side of the filter disc, etc), the pressure in the system will continue to drop very slowly even after closing both taps. In such cases, it is recommended that a T-piece be fitted between manostat and manometer; to one end of this T-piece is connected a piece of barometer tubing (internal diameter ~ 0.5 mm) with one end drawn out into a capillary. The

capillary should be narrow enough to ensure bleeding in of air into the system without producing a visible change in pressure. Such bleeding in of air will usually compensate completely for defects in the preparation of the manostat, and will ensure normal operation.

SUMMARY

Descriptions are given of a simple and convenient manostat and receiver, respectively, for analytical distillations on rectifying columns under vacuum; their operation is also described.

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BRIEF COMMUNICATIONS

THE USE OF CHROMATOGRAPHY IN QUALITATIVE ANALYSIS

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Detection of Mn^{2+} in the Presence of Cr^{3+}. During detection of small amounts of Mn^{2+} with hypobromite in the presence of Cu^{2+} as a catalyst, the color from the manganese is masked by the yellow color of the CrO_4^{2-} ions formed.

Tests which we carried out showed that satisfactory results can be obtained by the following method: 0.05 ml of test solution, acidified to 0.6% HCl, is passed through a micro-column packed with Al_2O_3 containing a 10% mixture of KBr and $KBrO_3$ (1:1). After some time (4-5 minutes) a brown strip of MnO_2 appears in the middle of the wide yellow band. If the 0.05 ml of solution contains 0.0035 mg of Mn, then after 10 minutes, only a weak brown color of MnO_2 is formed. On heating the column with an electric lamp (60 watt), the brown color of MnO_2 appears at even lower amounts of manganese (0.0017 mg Mn in 0.05 ml).

Micro-Analytical Detection of Co^{2+} in Admixture with Fe^{2+}, Fe^{3+}, Ni^{2+}, Mn^{2+}, Cr^{3+}, Zn^{2+}, Al^{3+}. Through a micro-column packed with Al_2O_3 is passed successively 0.05 ml of test solution, 2-3 drops of a saturated solution of NH_4SCN and 2-3 drops of acetone. After several minutes a blue ring appears if Co^{2+} is present. The limit of identification is 0.4 γ Co. The reaction sensitivity depends on NH_4SCN concentration; with decreasing NH_4SCN concentration, the sensitivity drops off.

Co^{2+} can be detected in a neutral solution in 5-7 minutes; in acid solution it takes 10-12 minutes.

Co^{2+} should be detected in neutral solution, when the red color of Fe^{3+} hardly appears and the blue band is clearly defined.

In acid solution a rather intense red color develops which may interfere with Co^{2+} detection; accordingly, when working with acid solutions, it is necessary to use a mixture of Al_2O_3 plus NaF in a ratio of from 1:8 to 1:10. In such cases, the red color does not appear even at HCl concentrations up to 2%. The reaction sensitivity however drops to 1.5 γ.

THE DICHROMATE METHOD OF DETERMINING PIPERAZINE

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In Castiglioni and Nivoli's paper [1], a method is described for the quantitative determination of piperazine as its slightly soluble bichromate salt. According to tests we have carried out, this method is capable of giving good results which are in agreement with results of the picrate method [2], as long as the following modifications are introduced:

1. Castiglioni and Nivoli state that piperazine dichromate has the following composition: $C_4H_8N_2 \cdot Cr_2O_7$. The formula $C_4H_{10}N_2 \cdot H_2Cr_2O_7$ is however more probable for piperazine dichromate — by analogy with other compounds of this type. This formula has been confirmed by the results of elemental analysis and by spectroscopic studies.

In order to decide on the correctness of one formula or the other for piperazine dichromate, the hydrogen content of the latter is of decisive importance. Castiglioni and Nivoli's formula indicates that piperazine dichromate contains 8 hydrogen atoms, while the formula $C_4H_{10}N_2 \cdot H_2Cr_2O_7$ contains 12 hydrogen atoms. At the same time, the content of the other elements depends only to a very small extent on the two formulas for the composition of piperazine dichromate; since, in this case the molecular weights according to the two formulas are 300.14 and 304.172, in which the difference is small. The results given in Castiglioni and Nivoli's article for the determination of nitrogen and chromic oxide can hardly be accepted as sufficient for a final decision as to which formula is correct, since the difference in the nitrogen content amounts to only 0.11%, while that in the Cr_2O_3 contents amounts to 0.67%. The following results were obtained during the determination of the hydrogen and carbon contents:

Found %: H 3.89; 3.93; 3.96; C 15.61; 15.80; 15.75.
Calculated for $C_4H_8N_2 \cdot Cr_2O_7$ %: H 2.69; C 16.01.
Calculated for $C_4H_{10}N_2 \cdot H_2Cr_2O_7$ %: H 3.98; C 15.79.

Comparison of the infra-red spectra of piperazine and piperazine dichromate carried out by coworker Yu. N. Sheinker of our Institute, showed that in the spectrum of piperazine at 1600 cm^{-1}, absorption bands appear which are characteristic of the NH_2^+ group, and are determined by the deformation vibrations of hydrogen atoms in it. The formation of the group $>N^+<^H_H$ is normal for the formation of the salts of organic bases, and, accordingly, is in good agreement with the formula suggested by us. At the same time, when such a group is present, it is difficult to visualize the piperazine derivative as having a formula of $C_4H_8N_2 \cdot Cr_2O_7$.

2. The conversion factor used by Castiglioni and Nivoli for converting the dichromate to piperazine is 0.2802. The numerical value given for this factor is quite incomprehensible even when one used their assumed formula of $C_4H_8N_2 \cdot Cr_2O_7$. In our opinion, the conversion factor to anhydrous piperazine should be 0.2832, and to the hexahydrate of piperazine — 0.6386.

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3. When working with 10% solutions of piperazine hexahydrate, the length for which the solutions are kept after addition of chromic acid can be cut down from 6-7 hours to 15 minutes. For this purpose, it is necessary to use 2 ml of solution (40 g CrO_3 in 100 ml water) and to cool the reaction mass in ice.

On applying the method indicated to the analysis of samples, the values found by the dichromate method for piperazine hexahydrate were 98.36 and 98.35%, while by the picrate method, the values found were 97.80 and 98.05%.

SUMMARY

Castiglioni and Nivoli's method for the determination of piperazine has been made more accurate.

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A FRACTIONAL REACTION FOR COBALT*

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In describing a fractional method for cobalt, the author of article [1], made several incorrect assumptions. According to him, the following cations do not interfere with the detection of cobalt:

$$NH_4^+, Li^+, K^+, Na^+, Rb^+, Cs^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Sr^{2+},$$

$$Fe^{2+}, Fe^{3+}, Zn^{2+}, Al^{3+}, Ni^{2+}, \qquad Cr^{3+}, Mn^{2+}, Ag^+, Hg^+, Hg^{2+},$$

$$Cu^{2+}, Pb^{3+}, Cd^{2+}, Bi^{3+}, Sn^{2+}, Sb^{3+}, Ce^{3+}, Zr^{4+}, UO_2^{2+}, Th^{4+}.$$
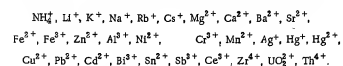
It is noted there, that of the cations listed, only Bi^{3+} which forms a "bright yellow or orange" complex with thiourea, masks the color of the complex compound of cobalt; copper also combines with thiourea to give a complex with a "white color", while nickel and chromium interfere because of their own intrinsic colors.

His statement does not correspond to facts, since, it is known that many cations form complexes with thiourea [2], and in doing so, use up reagent and lower the sensitivity of cobalt detection. Elements which react with thiourea, include the following:

$$Cu^{2+}, Mn^{2+}, Cd^{2+}, Ni^{2+}, Sn^{2+}, Zn^{2+}, Pb^{2+}, Ag^+, Hg^+, Hg^{2+}$$
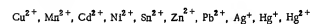
etc. Some of them, on interacting with thiourea form colored products, e.g. the compounds of univalent mercury: Hg_2Cl_2, Hg_2SO_4, $(HgNO_3)_2 \cdot 2H_2O$; mercuric oxide HgO and ferric chloride $FeCl_3 \cdot 6H_2O$ give an intensely black color; nickel chloride gives a yellow colored complex.

The shade and intensity of the color of reaction products containing the same cation, very often depend on the anion to which the cation to be tested for is connected [3]. The author also noted a difference in the shade of the blue-light blue color, obtained on triturating the various salts of cobalt with thiourea. Cobalt acetate forms reaction products having an intense ultramarine color; ferric sulfate and ferric alum a red-brown color, while nickel sulfate gives a dark blue complex with thiourea. The idea has originated of developing a so-called "molecular" qualitative analysis differing essentially from ordinary inorganic qualitative analysis carried out in solution. Using this new method of analysis it is now possible to diagnose not only individual cations and anions but frequently individual compounds and even the extent of hydration of crystals of one material.

The author follows the tradition of listing materials which interfere in the form of cations. This listing is, in principle, incorrect when it is applied to reactions between solid substances. It was noted above that the color depends on the anion also when salts of iron and nickel are triturated with thiourea. A similar relationship was also observed with other elements; thus, among the cations listed above, the chlorides of magnesium, calcium, aluminum, cerium, and to a lesser degree of ammonium, potassium, and strontium, in contrast to the nitrates, sulfates, phosphates and other salts of these elements will themselves interact with cobalt salts to form compounds which are colored blue in varying intensity. Accordingly, some of the chlorides just listed could well be used instead of thiourea.

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* Apropos Goldberg's article [1].

Chemical transformations between solid materials in their application to qualitative analysis has hardly been studied at all so far. There are results [3, 4, 5], which permit one to postulate that the simultaneous combination in an individual chemical material of physico-chemical properties characteristic of it, such as: solubility, hydration and dissociation, pH, "chemical nature","chemical specificity", determine its behavior during its trituration with other materials. All these properties are sharply expressed individually in a solid material: they direct the course of a chemical transformation, and sharply limit the use of so called "general" and "specific" reactions to the detection of a cation or an anion respectively to a particular salt only, or to that salt in a specific state of hydration. The interfering materials listed simply as ions cannot be regarded as correct.

SUMMARY

1. Compounds of univalent mercury, mercuric oxide, and the chlorides and sulfates of iron and nickel interfere with fractional detection of cobalt.

2. The visible color effect of the reaction depends on the anion with which the test cation is linked (the nature of the cation affects the color of the reaction product during detection of the anion).

3. Interferring materials should be referred to, not as ions, but as salts of a known chemical composition, when the method of trituration of powders is used for qualitative analytical purposes.

Received November 22, 1954

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* T. p. = Consultants Bureau Translation pagination.


A NEW INDICATOR — OXINE BLUE

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A large number of materials are known which have acid-base indicator properties; only a few of them however find practical application. This is explained by the rather strict requirements for indicators which are to be used for indicating a neutral end point [1]. Few good indicators are known for the weakly acid region. Even methyl orange and methyl red,the most widely used indicators in this range, fail to meet some of these requirements; the change in color from red to yellow during titration with alkalis lowers their value appreciably.

The synthesis and analytical properties of a new indicator — oxine blue — which can be used for neutralization purposes is described below.

Synthesis of the Indicator. 5.7 g of $HgCl_2$ and 50 ml of water are heated to the boil in a 250 ml flask. Excess NaOH is added (1.7 g in 30 ml H_2O). The freshly prepared HgO is washed a few times by decantation. To ~ 25 ml of the HgO suspension is added 1.1 g of Na_2CO_3. The solution is stirred with a stirrer until the sodium carbonate has dissolved completely. 1.84 g of p-diethylphenylenediamine sulfate dissolved in 10 ml H_2O is added, followed immediately by 1.02 g of 8-hydroxyquinoline in 50 ml C_2H_5OH. The whole is vigorously stirred for 1.5 hours while illuminated with a 300 watt lamp. 30 ml of C_2H_5OH is added and the bright blue solution filtered off from sediment; the precipitate is washed with alcohol. The filtrate is evaporated on a water bath. The resinous material is washed with 2 N NaOH, and 3-4 times with water. The product obtained is recrystallized from alcohol and dried in a desiccator over H_2SO_4; melting point 134- 135°; yield 2.29 g (81.2%).

This synthesis leads to the formation of the indicator — oxine blue (8-oxo-5-p-diethylaminophenylimino-5, 8-dihydroquinoline)
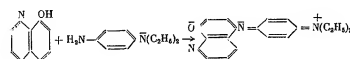

Simultaneously, apparently a byproduct is formed — 8-oxo-7-p-diethylaminophenylimino-5,8-dihydro-quinoline. For purification, the mixture is subjected to chromatographic separation on an Al_2O_3 column. The indicator passes through the column, while the by-product is held in the upper third of the layer; yield 67.0%.

Oxine blue has good indicator properties. The visible transition change for the indicator color, established with the aid of a series of buffer solutions and potentiometrically, was found to be 3.90-5.50 (4.70 pH).

The indicator shows a clear-cut color change: in acid solution it has bright orange color, while in alkali solution it is blue. It has been established that the salt and temperature effects for oxine blue are insignificant. Comparative titration of a strong acid with a weak base using oxine blue and methyl orange respectively as indicators, and also titration with phenolphthalein gave practically identical results.

Indicator solution is prepared by dissolving 0.25 g of oxine blue in C_2H_5OH. 4-5 drops of this solution in 100 ml of test solution are sufficient to give indicator properties.

The mechanism of the color change can be represented as a change from an inner-ionoid form (blue color) to an ionic acid form (orange color).
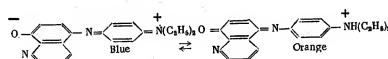
The author wishes to express his thanks to Prof. A. V. Kirsanov, on whose initiative, and under whose direction this work was carried out.

SUMMARY

The synthesis of oxine blue (8-oxo-5-p-diethylaminophenylimino-5,8-dihydroquinoline), which has good indicator properties, is described. The transition change for the indicator is at a pH of 3.90-5.00.

Received June 17, 1954

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DETECTION OF LEAD IN ORES BY THE TRITURATION METHOD

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Published methods [1-5], for detecting lead are not specific enough and require preliminary separation of lead from interfering elements. Recently an improved method for detecting lead has been suggested which is based on trituration of small amounts of its salts or ores first with potassium bisulfate, and subsequently with potassium iodide. When lead is present the mixture is colored yellow. Heating the triturated mixture speeds up appearance of the color. On treating the mixture with a drop of water, color intensity increases sharply. Of all reactions for lead based on the trituration method, the reaction with potassium iodide is the most suitable and reliable [6].

This method of trituration with KI has been checked on two different types of complex ores from the Primorsky deposits; results are described in the present communication.

Type A. A polymetallic ore containing up to 22 elements including SiO_2, Fe, Mn, Al, Ca, Mg, Pb, Zn, Bi, Cu and rare elements. Lead is chiefly in the form of the sulfide (lead content > 1%).

Type B. A complex ore, containing fluorite as the major component; upwards of 40 different elements are contained in it including: Ca, F, Al, Fe, Mg, Zn, Sn, Sb, B and rare elements. Lead is in the form of the sulfide in this ore also (lead content — hundredths of a percent). The color of the ore of both types varies from light grey to dark brown.

Tests showed that detection of lead without heating is only possible for Type A ores. The reaction. sensitivity in this case is not high. In order to determine the sensitivity of the method, test samples with a known lead content were successively diluted with amorphous silicic acid, and lead detected in the mixtures obtained. As an example, we have given in Table 1 the results for lead detection in one of the Type A ore samples.

TABLE 1

Ratio of ore to SiO_2 in mg		Pb content in %	Color after trituration
Ore	SiO_4		
5	—	17.4	Yellow
2.5	2.5	8.7	Yellow
1	4	3.4	Light yellow
0.5	4.5	1.7	Light yellow
0.25	5.75	0.35	Light yellow
0.12	4.88	0.42	Just observable traces
0.06	4.94	0.21	Not observed

Since the sensitivity of the method was not sufficient without heating, in a subsequent series of tests, the mixture, after trituration was heated for 1-2 minutes on an electric hot plate. Tests showed that it is best to add several drops of water, not just one. In order to lower the lead content in individual samples, the latter were diluted with amorphous silicic acid. Test samples which were mixed with silicic acid are designated in Table 2 with an asterisk.

The color intensity of the reaction product is linearly related to the lead content of the ore. The method permits determination of 0.0002% Pb, the sensitivity of the method is 200 times that of lead detection in solution with the help of K_2CrO_4. (According to the results of V. A. Nazarenko and N. S. Poluetkov [5], sensitivity of the detection of PbS in admixture with Pyrites amounts to 0.04%).

TABLE 2

Lead content		Ore type	Color after trituration
Percent or part of a percent	in %		
1% and over	22.64; 17.40; 15.90 14.70; 8.70; 11.70	A	Intensely yellow with a brownish shade
tenths of a %	0.84*; 0.78*; 0.65* 0.55*	A	Intense yellow, sometimes with a brownish shade
hundredths of a %	0.08*; 0.07*; 0.06*; 0.05* 0.052; 0.076; 0.021 0.031; 0.024	A B	Yellow
thousandths and ten thousandths of a %	0.005*; 0.002*; 0.001* 0.0008*; 0.0002*	B	Light yellow

Thus detection of lead by means of trituration with KI followed by heating is highly specific and sensitive. The reaction can be used for detection of lead not only in minerals and concentrates of lead, but also for the analysis of complex polymetallic and fluorite ores containing a large number of various elements.

Received February 11, 1955

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DETECTION OF FLUORINE IN MINERALS AND ORES BY A TRITURATION METHOD

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Fluorine in minerals is detected by etching of glass [1], or by the formation of volatile SiF_4 and its hydrolysis in a "suspended" water drop [2], by decolorization by means of the fluoride ion of red zirconium-alizarin lake [3], or the yellow-orange peroxide compound of titanium [4].

No methods have been published for the detection of fluorine by a trituration method [5]. The present communication is an attempt to fill this gap.

For the qualitative analysis of ores and minerals for fluorine by a trituration method, we used decolorization of ferric thiocyanate, which is used for the quantitative determination of fluorine in natural waters [6]. For this purpose the salt or mineral is triturated with $KHSO_4$, after which a little $FeCl_3$ is added, followed by 2-3 crystals of KSCN or NH_4SCN. Addition of small amounts of water speed the decolorization of thiocyanates. The reaction is very sensitive, and even insignificant amounts of fluorine decolorize ferric thiocyanate obtained by triturating 5-6 mg of $FeCl_3$ with 8 mg of KSCN. Table 1 contains results on the detection of fluorine in fluorides of second group metals. Lowering of the fluoride content was carried out by "dilution" with amorphous silicic acid.

TABLE 1

Salts	Decolorization of Fe(SCN)₃ for different fluoride contents (in %)				
	100	10	1.0	0.1	0.01
CaF_2	× × ×*	× × ×	× ×	× ×	× ×
CaF_2 (Mineral)	× × ×	× × ×	× ×	× ×	× ×
SrF_2	× ×	× ×	× ×	× ×	× ×
BaF_2	×	×	×	×	×

* Decolorization: × × × on prolonged trituration; × × for a short duration of trituration; × for insignificant duration of trituration.

Decolorization is most difficult to carry out in the case of calcium fluoride; decolorization is least difficult when the fluoride is that of barium; this, presumably is connected with the energy of the crystalling lattices of these salts.

The second series of tests were carried out with an ore from another Primorsky deposit; this ore contained significant amounts of fluorite and Fe, Al, Mg, Zn, Sn, and Pb as impurities.

* M. A. Rafienko and A. Ya. Vinogradova took part in the work.

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TABLE 2

Fluorine content In parts %	in %				Color of ferric thiocyanate
Tens	35.0	34.00	33.00	30.76	disappears
Units	3.5	3,4	3.3	3.08	"
Tenths	0.35	0.34	0.53	0.31	
Hundredths	0.035	0.034	0.033	0 031	remains a hardly distinguishable rose color

Preliminary tests showed that a large amount of sulfide sulfur can lead to decolorization of ferric thiocyanate during trituration of the ore with $KHSO_4$. In this case it is best to use a mixture of ammonium salts [5]. Table 2 contains results for detection of fluorine in this ore. Starting at one percent, the ore was diluted with amorphous silicic acid.

The reaction suggested is fairly sensitive and specific*. It should be pointed out that the method described by I. M. Isakov for detection of ferric oxide based on trituration of the mixture with KSCN or NH_4SCN is not applicable to ores containing fluorine.

Received October 28, 1954

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* The phosphate ion, gives a yellow-white precipitate of the phosphate $FePO_4$ [4], when the reaction is carried out in aqueous solution. On trituration of reagents with phosphates, decolorization of thiocyanates is not observed, since, apparently, iron phosphate is not formed under these conditions. Addition of water leads to a breakdown of the thiocyanate and to the separation of a precipitate of a light-yellow color which differs from K_3FeF_6.

ANATOLY KIPRILOVICH BABKO

(On His Fiftieth Birthday)

On the 15th of October 1955 Anatoly Kiprilovich Babko celebrated his fiftieth birthday, and, at the same time completed 25 years of scientific and teaching work; he is an outstanding Soviet chemist, a Corresponding Member of the Ukrainian SSR Academy of Sciences, a doctor of chemical sciences, and a professor.

A. K. Babko is well known as a scientist, working most successfully in the field of theoretical and practical analytical chemistry and the chemistry of complex compounds, as a skillful research worker, and a first class teacher. After completing his course in the Chemistry Faculty of Kiev Polytechnical Institute in 1927, he stayed on in the analytical section as an assistant, and at the same time studied for a higher degree under the direction of Professor N. A. Tananaev, who Babko regards as his teacher. In the last 10—15 years, a large amount of his work was carried out in conjunction with several of his pupils and coworkers.

Since 1931 Babko has been a lecturer in the Chemistry Faculty of Kiev Technological Institute of the Food Industry, and from 1934, a lecturer in the Department of Analytical Chemistry of Kiev State University. Since that time Babko has also carried out work in the Ukrainian Academy of Sciences.

In 1940 Babko defended his thesis for a doctorate; this thesis was fundamental work devoted to the equilibrium of complex-formation in aqueous solution. The original ideas on which this work was developed served as a basis for the further development of methods of physico-chemical analysis of complexes in solution—a field which he has successfully developed right up to the present time.

Since 1941 Babko has been the head of the Laboratory of Analytical Chemistry of the Institute of General and Inorganic Chemistry of the Ukrainian Academy of Sciences. In 1943 he was made a professor, while in 1944 he became the head of the Chair of Analytical Chemistry in Kiev State University; in 1948 he was made a Corresponding Member of the Ukrainian Academy of Sciences.

The scientific interests of Babko are wide and multifarious. Mention may be made of the following fields in which his scientific activity has led to particularly fruitful results: general questions of analytical chemistry; methods for the analysis of various materials; the use of complex compounds in colorimetry; and the chemistry of complex compounds.

From his early work in the field of general analytical chemistry, of particular interest is his derivation of a formula in 1935 for calculating the solubility of precipitates—salts of polybasic acids during their interaction with hydrogen ions, and also in the absence, and in the presence, respectively of excess of each of the precipitants. In the same year he published an article on the effect of pH on oxidation-reduction potentials; the general physico-chemical characteristics of the relation between oxidation-reduction processes and the acidity of the solution are also considered. Subsequently, a large amount of the work he carried out was devoted to the study of complex compounds. A study of alumino-silicate complexes showed how wrong many of the theories in vogue at the time were, with respect to the behavior of these complexes in solution.

At that time complex compounds started to attract the attention of analytical chemists, in view of the numerous possibilities they showed for use as precipitants, "masking" agents, colored compounds, etc. Nevertheless, despite the interest in these compounds, there were no clearly formulated ideas re the nature of dissociation, or about the methods for studying complex-formation equilibrium in solution. Individual methods which were occasionally useful had been suggested, such as the Abegg-Bodlender method, and the Ostromyslensky-Job method. Nevertheless when it came to applying these methods to the study of complex-formation in solution, there was much that was not clear. Babko must be credited with being the first in the Soviet Union to start a systematic investigation, on the basis of a physico-chemical study of complexes in solution by the light absorption method. In the course of this work he widely used the method of physico-chemical analysis. He demostrated the importance of the dissociation constant as an important characteristic of equilibrium in solution, developed the general position re step-wise dissociation, and ionic components of systems; and critically studied methods for determining the composition of complexes directly in solution. This work which continued over many years has now all been brought together in a monograph "The Physico-Chemical Analysis of Complex Compounds in Solution" (Acad. Sci. Press Ukrainian SSR, 1955).

From the investigations carried out by Babko to devlop methods of chemical analysis for practical purposes, use of the following types of reactions may be noted, e.g.,acid-base processes have been used for developing a colorimetric method of determining sodium carbonate in bicarbonate, volumetric methods of determining silicic acid, titration methods for silico fluorides, the lime method of determining alkaline metals in silicates. In the field of oxidation-reduction processes,one should mention Babko's work on the use of electrolytic metals as solid reducing agents (1937). He developed the bismuth reducer, which is included in a State Specification for analysis of iron ores. A reducing buret is described for the rapid and simple preparation of trivalent titanium solutions.

Of great importance is his work on the physico-chemical basis of colorimetric methods of analysis, on the application of organic reagents, and the scientifife foundation of the choice of optimum conditions for carrying out analytical determinations. He has derived equations relating formal deviations from Beer's law, the instability constant of the colored complex, and the concentrations of reactants. A vast amount of work has been carried out by him on colored thiocyanate complexes, on the salicylate and pyrocatechinate complexes of many metals and on dithizonates, dimethylglyoximates, and other complexes. This work, together with published results, served as a basis for the development of the fundamental precepts of colorimetric analysis. In 1951, in conjunction with A.T. Pilipenko, he published a book "Colorimetric Analysis," in which recommended methods of colorimetric analysis were given a serious fundamental basis.

In recent years Babko and his coworkers have been working on the analytical chemistry of rare metals, colorimetric methods of determining traces of non-metals, and determination of micro amounts of impurities in heat resistant alloys etc.

During his years of scientific activity Babko and his coworkers have carried out more than 125 projects which are a contribution to the development of analytical chemistry, chemical control of production, and the chemistry of complex compounds. All this work represents a new page in the theory of analytical chemistry and in the theory and practice of physico-chemical analysis of complexes in solution.

Babko has devoted a lot of his energies to training new cadres of Soviet scientists. Babko's lectures on qualitative and quantitative analysis, on the methods of physico-chemical analysis, and his special courses on the theoretical basis of analytical chemistry are very popular with the students at Kiev State University. His wide knowledge, the ability to impart his knowledge to others, his mastery of experimental technique, the demands he makes on himself, his coworkers and his pupils, have enabled Babko to create a school of analytical chemists.

His activity extends well beyond the confines of scientific research in the laboratory and his lectures. He is well known to Soviet chemists as a lecturer at many chemical meetings and conferences, and as a consultant on various questions of analytical chemistry and chemical control of production. While working in Kiev, A. K. Babko represents with honour Ukrainian Chemists, he has successfully developed chemical science together with other brotherly republics of the USSR.

For his successfull scientific and scientific-organization work Babko has been awarded the Order of Lenin, The Mark of Honour and the Medal "For Glorious Work in the Great War 1941—1945."

At the present time, Babko, a leading Soviet scientist,is energetically and with inspiration continuing his creative scientific, teaching, and general activity.

CHRONICLE

CONFERENCE HELD IN GORKY STATE UNIVERSITY ON THE APPLICATION OF LABELED ATOMS IN CHEMISTRY

During 21-24th of December 1955 a conference on the use of labeled atoms in chemistry organized by Gorky State University, was held; more than 200 participated in this conference, including scientific workers from Moscow, Leningrad, Kazan and other cities, factory workers, and teachers and scientific workers from Gorky and district. 34 papers were delivered at three plenary and six section meetings.

Opening the conference, the rector of the University V. 1. Shuirokov noted that the application of labeled atoms is one of the most important fields of the use of atomic energy for peaceful purposes, and pointed out that Gorky State University has accumulated considerable experience in the application of radioactive and stable isotopes in chemical research. 1. A. Korshunov and 1. M. Korenman in a plenary session gave a detailed review of fundamental research carried out with labeled atoms.

A group of reports in the section of radiochemistry and physical chemistry was devoted to the study of the application of the isotope effect to velocity constants of the hydrolysis of several carboxylic esters (1. A. Korshunov, N. F. Novtorov), to the vapor pressure of multi-atomic molecules (G. G. Devyatykh), to the mutual solubility of liquid deutero compounds (I.B.Rabinovich, V. D. Fedorova). The reports of N. N. Tunitsky (The Karpov Institute of Chemistry, Moscow), B. P. Nikolsky (Leningrad University), G. G. Devyatykh, V. A. Shushunov, B. Z. Torlin (Moscow), A. D. Zorin, N. I. Nikolaev, M. K. Shchennikova, B. G. Zateev were devoted to isotope separation. Results of studies on the state of radioactive phosphorus in targets after irradiation with neutrons were given in the reports of I. A. Korshunov and A. I. Shafiev. Investigation of the state of niobium and zirconium in solution was the object of the report of V. 1. Paramonova, A. S. Voevodsky, and V. V. Kolychev (Leningrad University). M. B. Neuman and V. B. Miller's report touched on the use of labeled atoms for studying the mechanism of complex reactions.

A. M. Petrov reported his findings on the adsorption of metals from solutions of their salts by various materials; while B. M. Noskov read a report on the study of diffusion and interatomic reactions in crystals. I. A. Korshunov and N. F. Novotorov reported the synthesis of organic compounds labeled with a radioactive carbon isotope.

One of the sessions on analytical chemistry was devoted to a consideration of coprecipitation. In the report of 1. M. Korenman, A. A. Tumanov, Z. I. Glazunov, Z. V. Krainova, and M. N. Baryshnikova, information was given on the study of the mechanism of coprecipitation with precipitates, obtained by the action of organic precipitants (hydroxyquinoline, anthranilic acid, antipyrine, and pyridine). This question was also touched upon in the report of 1. M. Korenman, P. A. Ganichev, and G. A. Shatalina (precipitation of picrates and dipicrylaminates). I. M. Korenman and M. N. Baryshnikov, communicated on the coprecipitation of micro-amounts of zinc, cadmium, and mercury with a precipitate of anthranilic acid. N. A. Rudnev (Moscow, Institute of Geochemistry and Analytical Chemistry) communicated on the elimination, or diminution of coprecipitation, of a number of cations with sulfide precipitates, on addition of surface active agents.

The reports of 1. M. Korenman, F. R. Sheyanova, and V. V. Korolikhin touched on the use of radioactive indicators for studying extraction of inner complex compounds. I. M. Korenman and F. R. Sheyanova's report was devoted to the use of non-isotope indicators for determining the solubility of certain salts. Determination of the solubility of carbon dioxide by the method of isotope dilution was the theme of the report given by M. K. Shchennikova, G. G. Devyatikh, and I. A. Korshunov. 1. M. Koreman and E. I. Zorin reported a rapid method

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for determining cadmium by measuring its natural radioactivity. N. P. Drozdov and A. N. Popov's report touched on the use of radio sulfur for determining the content of sulfonate groups in sulfonated coal. N. P. Drozdov and E. I. Paveleva's report was devoted to the radiographical method of analysis.

In the final plenary session, reports by I. A. Korenman, N. F. Novotorov, and A. I. Shafiev were heard on methods of determining the activity of solid and liquid preparations, and also on methods of determining the activity of compounds containing radioactive carbon. The question of safety during working with labeled atoms was discussed in the report of A. M. Petrov. Practically all the reports led to lively discussion.

In this short note it is impossible to give full justice to each of the reports; nevertheless, the list of reports given above show what a large number of questions were discussed at the conference, which were connected with the use of radioactive indicators in chemistry.

The conference adopted a resolution approving the initiative of the Gorky State University in calling this conference; the need for calling similar conferences periodically is pointed out. The resolution also notes the work carried out in Gorky State University on the use of labeled atoms in chemistry. The resolution also recommends that chemical laboratories and industrial enterprises in Gorky should use labeled atoms on a wider scale in their work.

I. M. Korenman

ANNOUNCEMENT

The Commission on Analytical Chemistry of the V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry, USSR Academy of Sciences, are getting ready to print a collection of articles on spectrophotometric and colorimetric method of analysis, amounting to about 30 pages compiled from material given at the All-Union Conference held on the 15-17 December 1955.

The collection will include review articles devoted to the present position of analysis on light absorption (descriptions of current analytical methods, apparatus used, and their prospective development), and also original articles on the theory and practical application of spectorphotometric and colorimetric methods of analysis for studying the processes of complex formation in solution, establishing molecular structure, determining the composition and dissociation constants of complex compounds, and identification of materials from their absorption spectra.

The collection includes articles devoted to determination of small concentrations of elements in pure metals and alloys, in natural water, etc., and also papers on the determination of organic compounds using the infra-red.

A number of articles are devoted to a description of practical methods of analysis and the apparatus used, and also to descriptions of improvements to apparatus used in the methods.

It is proposed to publish this collection in the first quarter of 1957.

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